THERMAL REORGANIZATION
AND
SECONDARY DEUTERIUM ISOTOPE EFFECT STUDIES
OF
SMALL RING COMPOUNDS

by

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A DISSERTATION PRESENTED TO THE GRADUATE COUNCIL OF
THE UNIVERSITY OF FLORIDA
IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE
DEGREE OF DOCTOR OF PHILOSOPHY

UNIVERSITY OF FLORIDA
1973

DEDICATION

To my parents, family and wife.

ACKNOWLEDGMENTS

The author wishes to acknowledge the financial support of the Ford Foundation-Universidad del Valle fellowship during the first two years of his graduate studies, financial assistance as provided by the Graduate School of the University of Florida in the form of a teaching assistantship for one year, and the research assistantship financed by the National Science Foundation for two years.

The author also wishes to express his sincere appreciation to Dr. W. R. Dolbier, Jr., his research director, for all the encouragement, guidance, suggestions and advice throughout the period of this research program.

The author extends his appreciation to the members of his supervisory committee. The author is also thankful to the members of his research group and classmates who made his stay at the University of Florida most enjoyable.

The author's wife, Rebecca Ann, deserves special thanks for her helpful assistance in preparing and typing this manuscript.

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Abstract of Dissertation Presented to the
Graduate Council of the University of Florida in Partial
Fulfillment of the Requirements for the Degree
of Doctor of Philosophy

THERMAL REORGANIZATION AND SECONDARY DEUTERIUM ISOTOPE
EFFECT STUDIES OF SMALL RING COMPOUNDS

by

Jorge H. Alonso

March, 1973

Chairman: W. R. Dolbier, Jr.
Major Department: Chemistry

Three topics were investigated:

1) The synthesis of dideuteriobiscyclopropylidene is reported and its thermal reorganization investigated. The intramolecular isotope effects for the ring opening step and for the cyclization step were determined from nmr analyses of the dideuterated methylenespiropentane products obtained. The ring opening isotope effect k_H/k_D was found to be 1.243 ±0.035 and the cyclization isotope effect k_H/k_D was found to be 1.136±0.016. The most satisfactory rationalization of these results requires a diradical intermediate and transition states that do not resemble and are less crowded than either product or starting material.

2) The synthesis of 1,1-divinylcyclopropanes d_0, d_2 and d_4 are reported. The activation parameters for the thermal reorganization of the undeuterated 1,1-divinylcyclopropane were determined. The intramolecular isotope effect k_H/k_D determined from the thermal reorganization of 1,1-divinylcylopropane d_2 was found to be 1.062 ± 0.018 and was estimated from nmr analysis of the dideuterated 1-vinylcyclopentene products. The intermolecular isotope effect k_H/k_D was estimated from the rate constant ratio of undeuterated and tetra deuterated 1,1-divinylcyclopropanes and was found to be 1.08 ± 0.07. A multistep process is favored on the basis of the isotope effects observed.

3) A novel base-catalyzed ring expansion of some cyclopropylcarbinyl derivatives to the cyclobutene derivatives was also investigated.

CHAPTER I

THERMAL REORGANIZATION OF DIDEUTERIOBISCYCLOPROPYLIDENE

Introduction

Secondary deuterium isotope effect studies have been increasingly used in recent years by physical organic chemists in an effort to clarify reaction mechanisms. Rationalization of the results obtained has been related to rehybridization changes,[1] steric interactions,[2] hyperconjugation[3] and inductive effects,[4] their use depending on which concept better explained the experimental data.

Isotope effects derive from changes in force constants concerning the vibrational frequencies at the deuterated position in the process of converting reactant to transition state. A normal isotope effect $K_H/k_D > 1$ would be observed if there were a decrease in vibrational frequency at the deuterated position going from reactant to transition state.[1] An inverse isotope effect $k_H/k_D < 1$ would be observed if there were an increase in vibrational frequency in the same process. Streitweiser and coworkers[1] made an analysis of the α-deuterium isotope effect on an S_N1 reaction based on statistical mechanics and indicated that the isotope effect was due predominantly to the change of a tetrahedral C-H bending

vibration to an out-of-plane deformation in the transition state.

That secondary deuterium isotope effects may be entirely steric in origin has also been suggested by other investigators[2,5] who have ascribed small inverse isotope effects to the effectively small size of the C-D bond relative to the C-H bond. Therefore a reaction that passes through a transition state that is sterically more strained than the reactant should give an inverse isotope effect $k_H/k_D<1$. Bartell[2] has strongly related steric and force constant change terminologies by using a harmonic approximation.

Crawford and Cameron[6] reported a normal isotope effect for the cyclization or biradical destruction of trimethylenemethane and indicated that such an effect may arise from the ponderal effect of the deuterium, as the CD_2 group will have twice the moment of inertia of the CH_2 group. This isotope effect study remained relatively isolated and uncorrelated until the recent isotope effect studies on allene (2+2) cycloadditions by Dolbier and Dai.[7] It was also pointed out[7] in the study of secondary deuterium isotope effects in allene cycloadditions that the transition state for product formation in a two-step process may actually have little or no bond character and that any observed isotope effect for such a process might be relief of nonbonded interactions and torsional interactions which would be found in a planar allylic radical system, but not in a nonplanar one. Such an isotope effect would be considered a "steric" isotope effect whereby

the hydrogen would rotate more rapidly out of a sterically congested situation.[8] From these studies much insight has been gained as to the nature and predictability of such isotope effects and has increased their credibility as a mechanistic tool in distinguishing stepwise from concerted cycloadditions.

Little use of secondary deuterium isotope effects in the study of thermal reorganizations has been previously attempted.[9] It is then of special interest to be able to compare the nature of the isotope effects in thermal reorganizations with those obtained from cycloadditions, especially in those cases where diradicals are thought to be involved, in order to acquire more knowledge about the nature of the intermediates as derived from different processes.

Very few molecules with the biscyclopropylidene structure have been investigated with respect to their thermal reorganization. The conversion of biscyclopropylidenes to methylenespiropentanes and the equilibration of methylenespiropentanes seem to bear a very close analogy to the mechanisns of simple methylenecyclopropane rearrangements which have been significantly elucidated in recent years and such reactions still generate much interest.

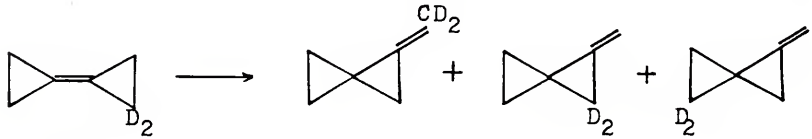
There has been considerable literature on the possible intermediacy of trimethylenemethane diradicals in the bicyclopropylidene rearrangement and most recently there has been much discussion as to the importance of nonplanar trimethylenemethane species in the methylenecyclopropane rearrangement.[10c]

Dewar has recently determined that the singlet parent trimethylenemethane species should be most stable in a nonplanar conformation.[11] Hückel calculations back up the nonplanarity of substituted trimethylenemethane diradicals[7] and accordingly the thermal conversion of substituted biscyclopropylidenes can be satisfactorily rationalized only by invoking nonplanar diradicals.[10c]

The probable intermediacy of nonplanar diradicals raises questions concerning the nature of transition states for bond-breaking processes leading to such intermediates and bond-forming processes which destroy them. We believe that secondary deuterium isotope effects may provide insight into these processes. Such isotope effects have never been obtained for the methylenecyclopropane rearrangement.

Results

In the thermal reorganization of dideuteriobiscyclopropylidene three products should be formed irreversibly and without interconversion. The ratio z/x+y will provide a measure of (k_H/k_D)intra for the rate-determining ring cleavage process while the ratio x/y will be a measure of (k_H/k_D)intra for the product-forming cyclization. In this

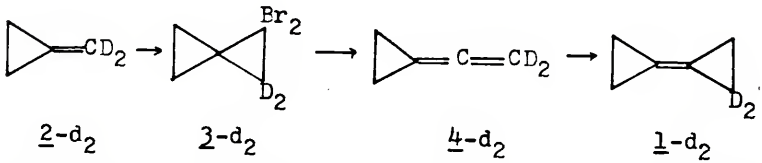


1-d2 x y z

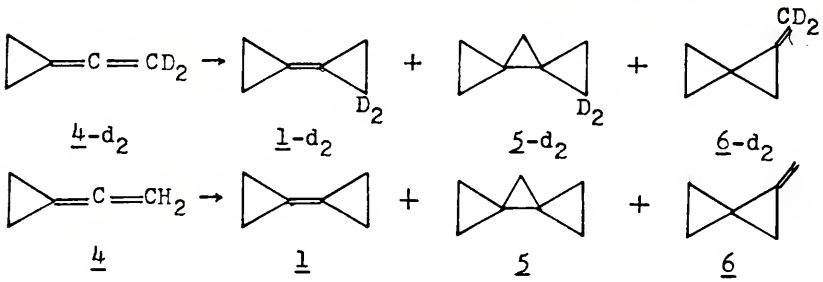
section we report the synthesis of dideuteriobiscyclopropylidene (1-d_2), its thermal reorganization and isotope effect studies.

Synthesis of Dideuteriobiscyclopropylidene (1-d_2)

The synthesis was accomplished following a scheme analogous to the one reported for the preparation of biscyclopropylidene (1).[10a] The last step in the synthesis, which offered some difficulties, produced also methylenespiropentane-d_2 (6-d_2) and dispiro (2.1.2.0) heptane-d_2 (5-d_2) when



using modified Simmons-Smith reaction conditions.[12] Spectral analysis (Table I) along with comparison of the gas chromatographic retention times with the undeuterated compounds,



obtained in a parallel reaction, confirmed the structures of the deuterated compounds.

The preparation of dideuteriomethylenecyclopropane (2-d_2) was accomplished by a series of straightforward reactions via the deuterated alcohol 7-d_2 and deuterated

Table I

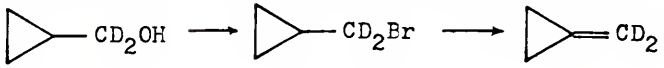
Chemical shift comparison for undeuterated and deuterated compounds

2	CCl_4[a]	δ1.03	triplet, 4H
		δ5.37	quintuplet, 2H
2-d_2	CCl_4	δ1.03	broad singlet
4	CCl_4	δ1.49	triplet, 4H
		δ4.73	quintuplet, 2H
4-d_2	CCl_4	δ1.49	broad singlet
1	C_6D_6[b]	δ1.25	sharp singlet
1-d_2	C_6D_6	δ1.25	broad singlet
3	CCl_4	δ1.24	singlet, 4H
		δ1.97	singlet, 2H
3-d_2	CCl_4	δ1.24	singlet

a = TMS was the internal standard for nmr's taken in CCl_4

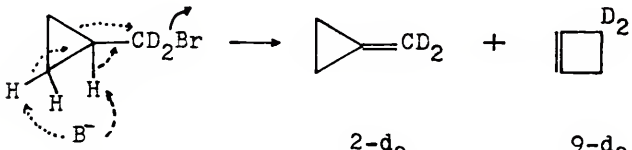
b = chemical shift taking δ7.24 for benzene

bromide 8-d_2. The dehydrohalogenation proceeded in good yield and 2-d_2 was used for the dibromocarbene reaction



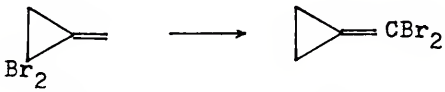
7-d_2 8-d_2 2-d_2

without further purification. A pilot small-scale reaction of the dehydrohalogenation step indicated that dideuteriomethylenecyclopropane (2-d_2) is produced in 80-90% yield along with dideuteriocyclobutene (9-d_2) that is apparently formed from abstraction by base of the hydrogen attached to the γ carbon in the cyclopropyl ring, as discussed in Chapter IV.



2-d_2 9-d_2

A previous attempt to prepare dideuteriobiscyclopropylidene (1-d_2) via the deuterated reduction of compound 10 generated from allene and dibromocarbene was made. The preparation was discontinued due to the very low conversion and difficulty in purifying 10, which was observed to isomerize to the novel compound 11 during distillation or when injected into a thirteen-foot preparative chromatographic Carbowax column at 160°.



10 11

Thermal Reorganization of Biscyclopropylidene (1)

LePerchec and Conia reported the reorganization of undeuterated biscyclopropylidene (1)[10a] at 210° and observed some dimerization. We thermolyzed 20-30 mg samples of biscyclopropylidene (1) at 214±2° under vacuum, in a 200 ml sealed tube which also contained 0.5 ml of benzene or pentane to minimize dimerization, and we observed no dimerization. The product of the reaction, methylenespiropentane (6), was characterized by its spectral analyses. It is worth noting that the nmr of methylenespiropentane (6)[10c] in CCl_4 gives a spectrum which does not show completely separated cyclopropyl and allyl hydrogens, while in C_6D_6 the cyclopropyl and allyl hydrogens are separated by 21.7 cps which facilitates their integration and that of the products of the thermal reorganization of dideuteriobiscyclopropylidene (1-d_2).

Thermal Reorganization of Dideuteriobiscyclopropylidene

Three independent samples of dideuteriobiscyclopropylidene (1-d_2) were pyrolyzed at 214±2° for forty-nine hours. The ratio of x, y and z products was determined by nmr analysis from the integration of the cyclopropyl hydrogens A, allylic hydrogens B and vinylic hydrogens C. By solving the three algebraic equations a through c we found x, y and z.

a) $4x + 4y + 2z = A$ $\qquad x = \frac{A + B - 2C}{6}$

b) $2x + 2z = B$ $\qquad y = \frac{A + C - 2B}{6}$

c) $2y + 2z = C$ $\qquad z = \frac{2B + 2C - A}{6}$

The ratios x/z and z/x+y were then easily obtained and the isotope effect determined.

$$\frac{x}{y} = \frac{A + B - 2C}{A + C - 2B} = k_H/k_D \text{ ring cyclization}$$

$$\frac{z}{x + y} = \frac{2B + 2C - A}{2A - B - C} = k_H/k_D \text{ ring cleavage}$$

Table II

Intramolecular isotope effects for the dideuteriobiscyclopropylidene thermal reorganization

Run	x/y	z/x+y
1	1.148	1.214
2	1.117	1.232
3	1.142	1.282
Average	1.136±0.016	1.243±0.035

Heating the reaction run 2 for ten more hours at 244° gave x/y = 1.028 and z/x+y = 1.230.

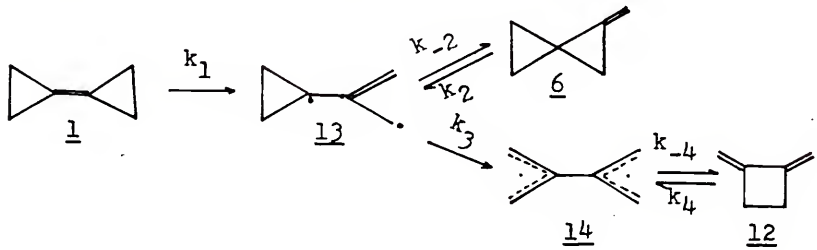
A control sample of undeuterated biscyclopropylidene (1) gave a ratio B/C = 1.001±0.012 and A/B+C = 0.997±0.013.

The error for the three independent runs is expressed as standard deviation. The nmr integrations of hydrogens A, B and C were repeated at least ten times for each run (spectrum 9). The maximum error of the nmr integrations expressed as standard deviation is ~1.3%.

Discussion

Biscyclopropylidene (1), methylenespiropentane (6) and 1,2-dimethylenecyclobutane (12) may in principle be interconverted[10c] via the pair of diradicals 13 and 14. The thermodynamic driving force is apparently strong in the direction 1→6 and in the direction 6→12, with a significant barrier between 13 and 14 (vide infra). Heating of 6 produced none

of 1, indicating that the equilibrium 1→6 lies far to the right. An energy surface figure that accommodates 1, 6 and 12 interconversion is found in the literature.[10c]



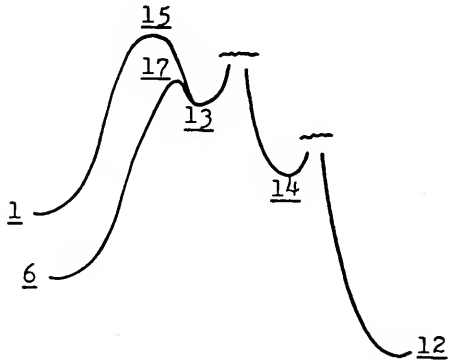
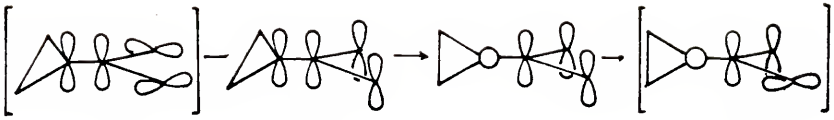


Figure 1. Energy surface for compounds 1, 6 and 12.

The transition state diradical 15, which is considerably less crowded than 1, would be formed upon ring cleavage of biscyclopropylidene 1, a very crowded molecule. An isotope effect $k_H/k_D>1$ should be expected for the ring cleavage based on steric arguments, and accordingly, we found an isotope effect $k_H/k_D = 1.243$. Once the cleavage has taken place, the diradical 15 may align itself to form the planar diradical 16 or the more stable orthogonal diradical intermediate 13, which is somewhat more crowded than 15 but still considerably less



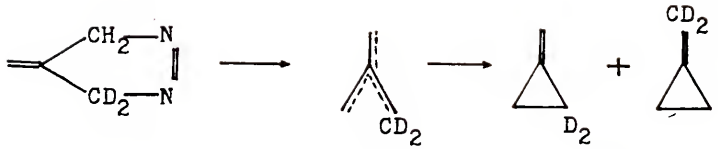
15 16 13 17

1 6

crowded than 1. Cyclization to obtain methylenespiropentane would require a 90° rotation of a methylene group. In such a process the transition state diradical 17, which is less crowded than 13, would be obtained. The ring cyclization process 13 → 17 should afford an isotope effect $k_H/k_D > 1$ as would be expected from Crawford and Cameron's work[6] on the ring cyclization of trimethylenemethane, from Dolbier and Dai's work,[7] and from our steric arguments. We observed an isotope effect $k_H/k_D = 1.136$ for the ring cyclization process.

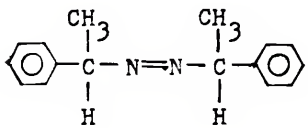
Some investigators follow the general thinking that the transition state has to resemble the starting materials or the products. What makes our system particularly interesting is that we are postulating a transition state that does not resemble, and is less crowded than, either product or starting material.

Our ring cyclization isotope effect $k_H/k_D = 1.136$ can be compared with Crawford and Cameron's[6] isotope effect $k_H/k_D = 1.37$ for the cyclization of trimethylenemethane (19), formed from the symmetrical breaking of the carbon-nitrogen bonds of 4-methylene-1-pyrazoline-3,3-d_2 (18). In Crawford and Cameron's system[6] there are two possible rotations for 19,



18 19 2-d_2

since in the planar trimethylenemethane two π orbitals must rotate to form a σ bond, while in our system only one orbital must rotate to form a σ bond. Our isotope effect should then be approximately the square root of Crawford and Cameron's isotope effect. This is essentially the case, since isotope effects are multiplicative. Seltzer's observation of a normal intermolecular isotope effect[13] k_H/k_D = 1.27 for the homolytic cleavage of carbon-nitrogen bonds in compounds 20 and 21 has some analogy to the intramolecular ring cleavage process of our dideuteriobiscyclopropylidene (1-d_2).



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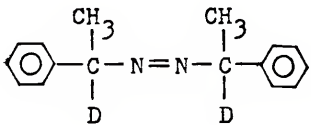


21

Change of hybridization in Seltzer's system, $sp^3 \rightarrow sp^2$, is more similar to Streitweiser's solvolytic isotope effect[1] studies than it is to our system, $sp^2 \rightarrow sp^2$ radical, but it is apparent that our steric argument seems to apply to Seltzer's system; the carbon-nitrogen bond breaks faster in compound 26 so as to relieve crowdedness in the starting material.

That the observed isotope effect in the thermal reorganization of dideuteriobiscyclopropylidene (1-d_2) is a kinetic isotope effect was proved by heating the sample used in run 2 for ten more hours at 244°. We observed that the ratio z/x+y remained essentially unaltered, while the ratio x/y decreased to 1.028, an indication that an equilibrium[7,14] between x and y was predominant at a higher temperature which reversed the reaction to the intermediate 13.

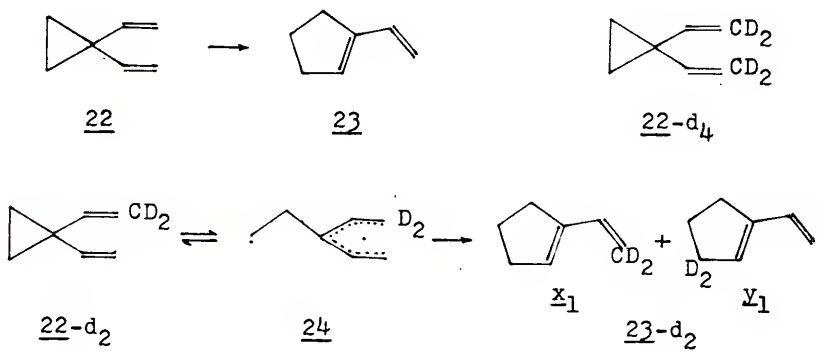
The magnitude of the secondary deuterium isotope effect that we have observed in the thermal reorganization of dideuteriobiscyclopropylidene (1-d_2) seems to exclude the possibility of a concerted mechanism. A concerted mechanism for which bond breaking is farther ahead than bond formation would be expected to give a ratio z/x+y 1 and a ratio x/y closer to 1 than the one we observed experimentally. A concerted mechanism for which bond formation in the transition state is appreciable would be expected to give a ratio x/y 1 by favoring y with the hydrogens in the vinylic position over the more crowded x with the hydrogens in the allylic position.

CHAPTER II

THERMAL REORGANIZATION OF 1,1-DIVINYLCYCLOPROPANE

Since the product-forming cyclization process of an intermediate diradical can give rise to a significant normal secondary deuterium isotope effect, it was our belief that the intermediacy of a diradical 24 in the conversion of 22→23 could be proved utilizing the dideuterated and tetra-deuterated species 22-d_2 and 22-d_4.

The ratio x_1/y_1 should provide a measure of (k_H/k_D)intra for the product-forming cyclization. The ratio of the rate constant for the thermolysis of 22 to the rate constant for the thermolysis of 22-d_4 should provide a measure of (k_H/k_D) inter for the ring cleavage process.

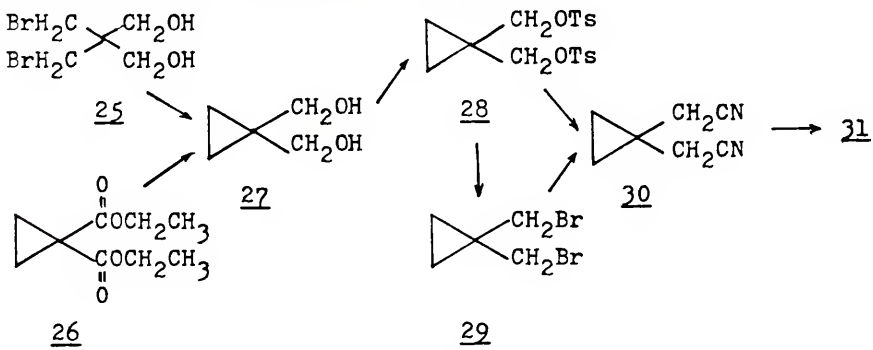


In this chapter we will discuss the synthesis and thermal reorganization of the novel 1,1-divinylcyclopropanes, intramolecular and intermolecular isotope effect studies, as well as the activation parameters of the conversion 22→23.

Results

Synthesis of Cyclopropane-1,1-diacetic Acid

Cyclopropane-1,1-diacetic acid (31), the starting material for the synthesis of the compounds 22, 22-d_2 and 22-d_4, was prepared according to a scheme analogous to the one reported by Chamboux and coworkers.[15]

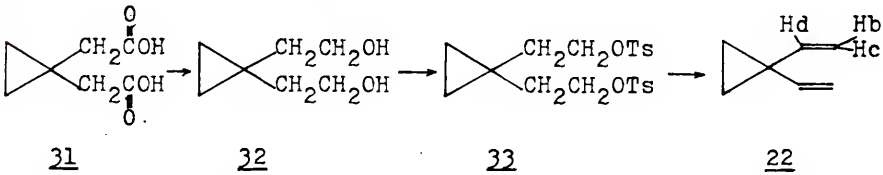


Cyclopropane-1,1-dicarbinol (27) was easily prepared by treating 2,2-bisbromomethyl-1,3-propanediol (25) with zinc in refluxing ethanol. Zinc dibromide, a by-product of this reaction, was complexed and separated by filtration by bubbling ammonia in the alcoholic solution at 0°. The $LiAlH_4$ reduction of compound 26 also produced 27 but the yield was lower. Tosylation of 27 produced the ditosylate 28. Treatment of 28 with LiBr in refluxing acetone formed the dibromide 29. Cyclopropane-1,1-dicarbonitrile 30 was generated from the

reaction of the ditosylate 28 or the dibromide 29 with potassium cyanide in dimethyl sulfoxide (DMSO) at 80°. The reaction with the dibromide 29 was cleaner and no decomposition was observed as in the case of ditosylate 28 which became dark and whose reaction product was difficult to work up. Hydrolysis of 30 smoothly produced cyclopropane-1,1-diacetic acid (31).

Synthesis of 1,1-Divinylcyclopropane

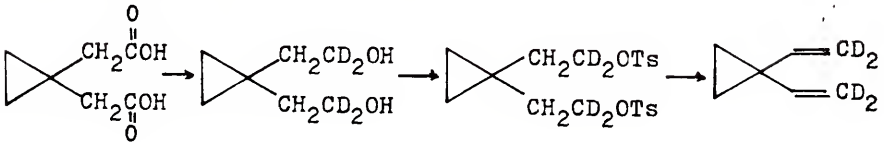
Via sequential (1) reduction by $LiAlH_4$, (2) tosylation, and (3) elimination using potassium tert-butoxide in DMSO at 26° we successfully prepared the novel 1,1-divinylcyclopropane 22. The yield for the elimination step was ~45%. The structure of 22 was verified by its nmr, ir, mass spectrum and analysis. The nmr (CCl_4) showed a sharp singlet at δ 0.79 (4H) as well as doublets at δ 4.89 (J_{bd} = 9.5, J_{bc} = 1.7 cps, 2H), δ 4.91 (J_{cd} = 18, J_{bc} = 1.7 cps, 2H), and δ 5.78 (J_{bd} = 9.5, J_{cd} = 18 cps, 2H); the ir spectrum showed strong peaks at 1639, 991 and 902 cm^{-1} and the mass spectrum at m/e 94 (P), 79 (base), 77 and 39.



Synthesis of 1,1-Divinylcyclopropane-d_4

A path similar to the one followed for the preparation of 22 easily afforded the novel compound 22-d_4, whose nmr showed a sharp singlet at δ 0.79 (4H) and a broad multiplet

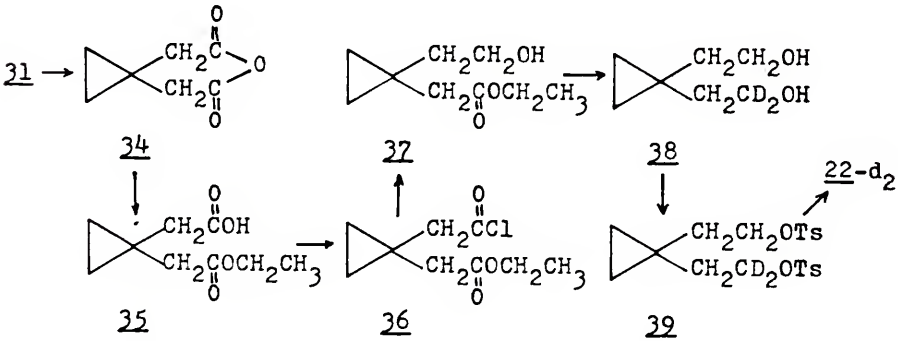
at δ 5.74 (2H); the ir showed peaks at 2967, 2326, 2222, 1590, 1010, 952-893 and 746-709 cm^{-1}.



31 32-d_4 33-d_4 22-d_4

Synthesis of 1,1-Divinylcyclopropane-d_2

The synthesis of the novel 1,1-divinylcyclopropane-d_2 (22-d_2) was successfully achieved by the following series of reactions:

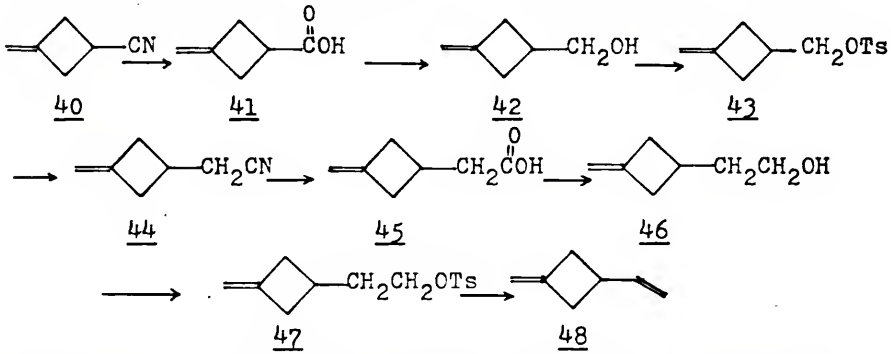


The key step in this synthesis was the selective reduction of the acyl halide group in 36 to an alcohol group in 37. By using[16] $NaBH_4$ in anhydrous dioxane, 37 was obtained in 42% yield.

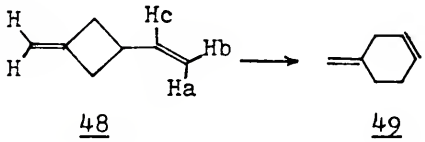
The nmr of 1,1-divinylcyclopropane-d_2 (22-d_2) in CCl_4 showed a sharp singlet at δ 0.79 (4H), doublets at δ 4.89 (1H) and δ 4.91 (1H), doublet of doublets at δ 5.78 combined with a broad multiplet at δ 5.74 (2H); the ir showed peaks at 3058, 2967, 2326, 2222, 1639, 1590, 1427, 991, 952-893, 736 and 725 cm^{-1}.

Synthesis of 3-Vinylmethylenecyclobutane

The usefulness of the sequence followed in the preparation of 1,1-divinylcyclopropane (22) was tested in the preparation of the novel 3-vinylmethylenecyclobutane (48) which offered special interest in diradical rearrangement studies. All of the steps followed for the preparation of 48 proceeded with high efficiency with the exception of the elimination step which gave 48 in ~40% yield. The structure of 48 was



verified by its spectral characteristics and by its smooth thermal reorganization to 4-methylenecyclohexene (49)[17] when a small sample of 48 was heated at 240° in a sealed tube for nine hours.



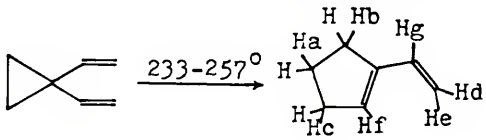
Thermal Reorganization of 1,1-Divinylcyclopropane

Compound 22 could be converted quantitatively at temperatures above 230° to 1-vinylcyclopentene (23)[18] whose nmr gave a broad doublet at δ 1.93 (2H), a broad multiplet at δ 2.30-

2.50 (4H), doublets at δ 4.94 (J_{dg} = 9.5, J_{de} = 2 cps, 1H) and δ 4.96 (J_{eg} = 18, J_{de} = 2 cps, 1H), a broad singlet at δ 5.62 (1H), and a doublet of doublets at δ 6.48 (J_{dg} = 9.5, J_{eg} = 18 cps, 1H); the ir spectrum showed strong peaks at 2924, 990 and 902 cm^{-1}; the uv had λmax 233 mμ (ϵ 22,400). The thermolysis of 22 was carried out in sealed tubes both in the gas phase and in dilute benzene or pentane solution to avoid any dimerization or polymerization.

Activation Parameters

The rate of disappearance of 22 in benzene solution using pentane as an internal standard was followed by gas chromatography using a ten-foot Carbowax column. The recorder of the gas chromatograph was attached to an Infotronics Digital Readout System model CRS-100 to facilitate and minimize the error in determining the peak areas.



22 23

The conversion 22 → 23, as in similar vinylcyclopropane rearrangements,[19] was unimolecular and a good Arrhenius plot was obtained in the temperature range studied. Least-squares analyses were performed to obtain the best fit of the data.

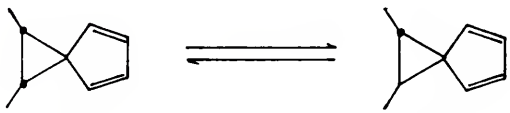
The activation parameters were calculated from the kinetic data: Ea = 39.6±1 kcal/mol; log A = 12.57; $\Delta H^{\ddagger}$ = 38.6 ±1 kcal/mol and $\Delta S^{\ddagger}$ = -2.8±4 cal/deg.

Table III

Kinetic data for thermal reorganization of 22

Temp (^{o}C)	Temp (^{o}K)	10^{-3}/Temp (^{o}K)	10^{-5} K(sec^{-1})
233.5	506.5	1.9743	3.148
242.0	515.0	1.9417	6.023
257.0	530.0	1.8868	18.342

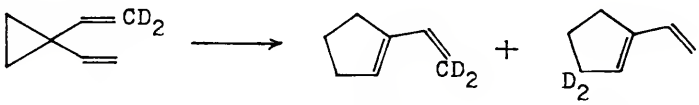
These results indicate that the addition of a second vinyl group lowers the activation energy for the vinylcyclopropane→cyclopentene rearrangement by 11-12 kcal/mol. The fact that one observes an activation energy lowering almost equal to that due to the presence of the first vinyl group (14 kcal/mol)[19] could be construed as being consistent with either a concerted process or the intermediacy of diradical species in the reaction. Our values may be compared with the values of Ea = 42.7 and log A = 14.76 for the geometrical isomerization of the spiroheptadiene 50.[20]



50 51

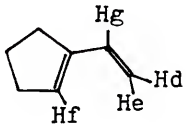
Intramolecular Isotope Effect

Five independent samples of 1,1-divinylcyclopropane-d_2 (22-d_2) were thermolyzed at 285° for twenty hours.



22-d_2 x_1 23-d_2 y_1

The relative amounts of compounds $\underline{x}_1$ and $\underline{y}_1$ were determined by nmr integrations of the vinyl hydrogens de, g and f in either deuterated benzene (C_6D_6) or CCl_4 for which the nmr resolution was slightly better.



The ratios of vinyl hydrogens f/de and g/de are directly related to the ratio x_1/y_1 and consequently to (k_H/k_D)intra for the ring cyclization process in the diradical mechanism.

Table IV

Intramolecular isotope effect for the thermal reorganization 22-d_2

Run	g/de	f/de
1	1.058±0.016	1.060±0.022
2	1.050±0.017	1.056±0.021
3	1.055±0.012	1.054±0.010
4	1.082±0.017	1.077±0.021
5	1.058±0.017	1.068±0.022

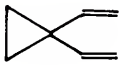
Average: 1.062±0.018

An nmr analysis control on the undeuterated 1-vinylcyclopentene (23) gave g/de = 0.5005±0.024 and f/de = 0.5005 ±0.012.

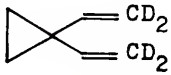
Intermolecular Isotope Effect

The ratio of the rate constants for 22 and 22-d_4 is directly related to (k_H/k_D)inter for the ring cleavage process

in the conversion 22→23. We simultaneously determined the rate constants for 22 and 22-d_4 at 242° and found (k_H/k_D) = 1.08±0.07.



22



22-d_4

Discussion

While the identity of the two secondary isotope effects could be interpreted as deriving from a common transition state for the rate-determining and the product-forming steps, and this may be equated with a concerted process, we do not favor this explanation. Most important, the preponderant weight of analogy insists that a rate-determining step process in which a sp^2 carbon is transformed into a sp^3 carbon should be associated with an inverse kinetic secondary deuterium isotope effect. The only possible exception to this observation is the yet anomalous ketene-styrene (2+2) study of Baldwin and Fleming.[21] In light of all past analogies we favor the interpretation of the results as an indication of a multistep process. In this case there are two possible pathways: rate-determining diradical formation or rate-determining diradical destruction.

In the former situation there is some analogy that a normal intermolecular isotope effect is to be expected for the conversion $sp^2 \rightarrow$ radical,[7,22] in which case our observed intermolecular isotope effect could be derived from a

rate-determining formation of the diradical 24. Thus our observed intramolecular isotope effect, while being relatively small,[7] can be understood as deriving from the product-forming destruction.

In the latter situation, a pre-equilibrium formation of diradical 24 could result in the rate-determining and product-forming transition states being one and the same. Thus the two isotope effects should be nearly identical and resembling in value those ordinarily observed for diradical cyclizations.[7]

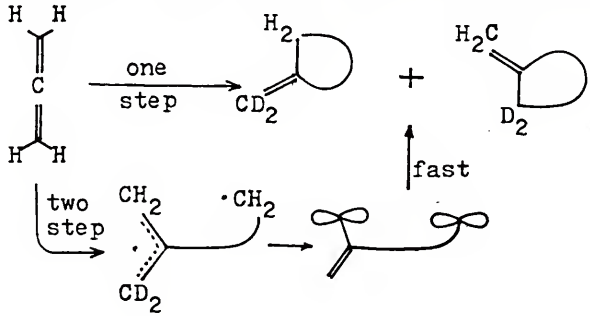
CHAPTER III

GENERAL CONCLUSIONS OF ISOTOPE EFFECT RESULTS

The determination of the nature of the intermediates in a stepwise reorganization process is very important in the elucidation of reaction mechanisms. From our experimental results in the biscyclopropylidene system it is apparent that changes in geometry leading to a transition state can be correlated with the isotope effects observed. Our results are consistent with previous studies of the secondary deuterium isotope effect in allene cycloadditions[7] and biradical destruction[6] that similarly have allylic intermediates.

Hybridization changes have been used sometimes as a tool for predicting isotope effects. Thus concerted cycloaddition reactions, where an increase in vibrational frequency at the deuterated position going from the reactant to product which result in k_H/k_D being <1 in both the intra- and intermolecular competitions, have been associated with a hybridization change $sp^2 \rightarrow sp^3$. The rate-determining step of a two-step mechanism involving no change in hybridization ($sp^2 \rightarrow sp^2$ radical) should give at best a small isotope effect. Pryor and coworker [22a] have demonstrated that the conversion $sp^2 \rightarrow sp^2$ radical not only should, but does, give rise to a small normal deuterium isotope effect, a fact that was also observed in Dolbier and Dai's cycloaddition studies.[7]

Intramolecular discrimination in the two-step process of a cycloaddition reaction takes place in a fast, relatively low activation energy step where the transition state should occur early along the reaction coordinate. Dolbier and Dai pointed out that a simple combination of radicals could be



52 53

thought to have negligible activation energy. Since their studies indicate that there is an apparent, small but significant, activation energy for combination of 52, this could derive from the rotation of a planar configuration toward the orthogonal geometry 53 that is necessary for bond formation. It was then suggested that the isotope effect observed should not be due to a change in hybridization but due to a relief of nonbonded interactions and torsional interactions which would be found in the planar allylic but not in the nonplanar radical system.[7]

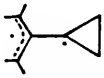
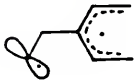
The normal isotope effect observed by Crawford and Cameron[6] for the destruction of the trimethylenemethane diradical remained uncorrelated until Dolbier and Dai's results on the ring closure of allylic diradicals.[7]

The correlation between changes of hybridization and isotope effects observed is at fault in some cases when the isotope effect studies are put together. In the ring closure step of the trimethylenemethane diradical a change of hybridization sp^2 radical$\rightarrow sp^2$ gave an appreciable normal isotope effect of 1.37, which would be anomalous if compared to Pryor and coworker's calculations which indicate that a change of hybridization $sp^2 \rightarrow sp^2$ radical should have a normal isotope effect.[22] The ring closure step in the two-step (2+2) cycloaddition reactions having a hybridization change sp^2 radical $\rightarrow sp^3$ has a normal isotope effect of 1.14-1.20. The isotope effect observed for the cyclization step (sp^2 radical$\rightarrow sp^2$) in our studies of the dideuteriobiscyclopropylidene thermal rearrangement, which has a trimethylenemethane environment, correlates well with Crawford and Cameron's results.[6] Our 1,1-divinylcyclopropane rearrangement gave an isotope effect of 1.062 for the cyclization step involving a hybridization change sp^2 radical$\rightarrow sp^3$. The ring cleavage process for our biscyclopropylidene rearrangement involved a hybridization change $sp^2 \rightarrow sp^2$ radical and a normal isotope effect of 1.243 was observed.

A comparison of the isotope effects of the cyclization process regardless of the hybridization changes shows an interesting similarity. As previously indicated, a possible source of isotope effects in the cyclization process which is also applicable to the ring-opening process might be relief of nonbonded interactions and torsional interactions also known as steric effect.

Table V

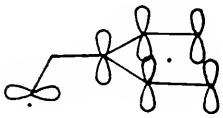
Isotope effects observed in cyclization studies

	k_H/k_D
	1.370
	1.136
	1.140-1.200
	1.062

In the cyclization of the parent trimethylenemethane diradical, which is probably planar, two π orbitals must rotate to form a σ bond giving rise to an appreciably large isotope effect of 1.370 based on steric considerations. In spite of the predicted inherent stability of the planar trimethylenemethane diradical it seems clear that any alkyl substitution is sufficient to prohibit planarity of the system. In the thermal rearrangement of dideuteriobiscyclopropylidene, the more stable orthogonal intermediate is favored and therefore only one π orbital must rotate to form a σ bond and give consequently a smaller isotope effect of 1.136. The transition states postulated in the rearrangement of dideuteriobiscyclopropylidene may have little or no bond character and are accordingly less crowded than either the starting material or the product. This argument and the

results obtained are in close agreement with the experimental results for the (2+2) reactions and dimerization of allenes in which allylic diradicals that do not resemble the product are suggested. The isotope effect observed is derived from the rotation of a methylene group from the planar configuration 52 toward the orthogonal geometry 53 which is necessary for σ bond formation.

The intramolecular isotope effects in the (2+2) allene cycloadditions[7] presented values varying from 1.140 to 1.200 which seem to be characteristic of the allyl radical. Our intramolecular isotope effect 1.062 for the conversion 22→23 could also be explained by assuming that the pentadienyl radical 24 does not have the same activation barrier of rotation as allyl radical 54. A lower activation barrier in 24 would be expected since rotation is made easier the longer the conjugation.



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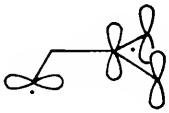


54

The real source of the secondary deuterium isotope effects is a change in the vibrational frequency at the deuterated position which appears to be closely related to a steric effect. In going from a very crowded configuration to a less crowded configuration a normal isotope effect should be observed. Such an effect was observed in Dolbier

and Dai's studies and in our thermal reorganization studies. Using the out-of-plane bending frequencies of methylenecyclopropane[23] as a model for biscyclopropylidene and the out-of-plane bending frequencies of methyl radical [24] as a best model for the orthogonal allyl radical transition state, after the fashion of Streitweiser,[1] the predicted direction of the isotope effect for the ring cleavage process is the same as that found in our experiments (Tables VI and VII).

Besides the hybridization effects and steric effects discussed previously, hyperconjugation and inductive effects have been hypothesized as possible origins of secondary deuterium isotope effects.

Inductive effects have been rationalized[4] on the interpretation that since the carbon-deuterium bond is shorter than the carbon-hydrogen bond, it will have a higher charge density and the deuterium will act as an electron-donating relative to hydrogen. Inductive effects are usually low and should be of minor importance in the thermal reorganization of biscyclopropylidene as has been the case for cycloaddition reactions.

Hyperconjugation and secondary β-deuterium isotope effects have been associated since Shiner[3] indicated that reactions with rate-determining steps that involve carbonium ion or partial carbonium ion formation are slowed down by the substitution of a deuterium atom for a hydrogen position in a hyperconjugative position. The possibility of having the carbon-hydrogen hyperconjugation resonance structure 55

Table VI

Observed frequencies of a planar methyl radical[24]

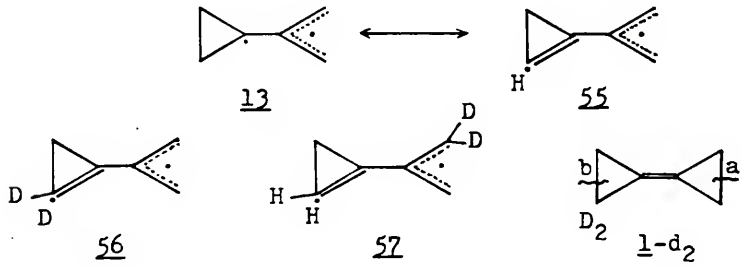
CH_3	730.3 cm^{-1}
CD_3	567.0 cm^{-1}

Table VII

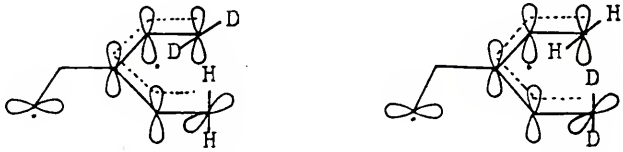
Infrared absorption frequencies of methylene cyclopropane d_0 and d_6[23]

Vibration	Form of Vibration	$C_4H_6(cm^{-1})$	$C_4D_6(cm^{-1})$
4	A_1 CH_2 deformation	1436.5	1168.0
15	B_1 CH_2 deformation	1410.0	1122.0
7	A_1 CH_2 wagging	1002.6	804.2
17	B_1 CH_2 wagging	1125.3	1017.0
21	B_2 CH_2 twisting	1073.0	835.5
23	B_2 CH_3 rocking	748.6	537.5

could be discarded, based on the fact that an inverse isotope effect would be observed for the ring cleavage of dideuteriobiscyclopropylidene (1-d_2), by favoring 57 over 56; or because the geometry for hyperconjugation is not favorable.[25]



Although hyperconjugation has been associated with β-secondary deuterium isotope effects,[3] a combination of hyperconjugative and inductive effects could be taken into consideration as an explanation for the intramolecular isotope effect observed in the cyclization step of the thermal reorganization of 1,1-divinylcyclopropane. Hydrogen, being more electronegative than deuterium, would tend to conjugate according to the pentadienyl radical structure 58 rather than 59 and then give rise to a normal isotope effect.

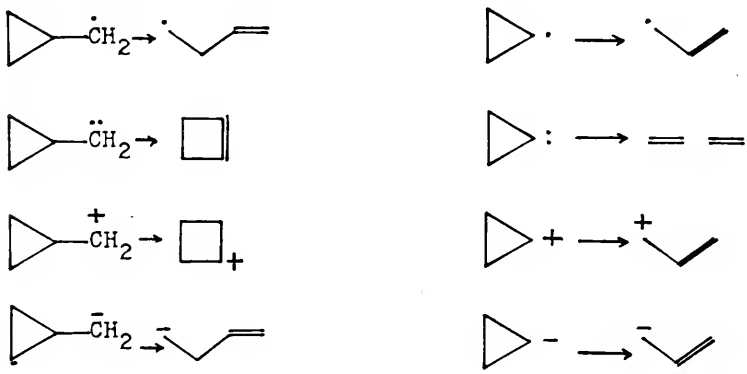


58 59

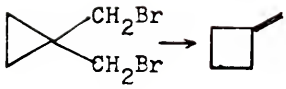
CHAPTER IV

BASE-CATALYZED ELIMINATION OF SMALL RING COMPOUNDS

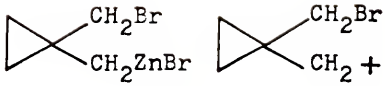
Ring expansion and ring opening products in the cyclopropylcarbinyl system as well as ring opening products in the cyclopropyl system have been reported in the literature.[26]



Ring expansions via anionic intermediates are less common. Slobodin and Shokhor[27] studied the reaction of 1,1-bisbromomethylcyclopropane (29) with zinc in ethanol solution and obtained methylenecyclobutane (60). Mechanisms for this reaction[28] have been suggested as a base-induced rearrangement with zinc metal acting as a base, an intermediate organozinc compound 61, or an electrophilically induced rearrangement via 62.

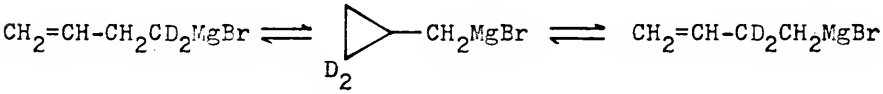


29 60



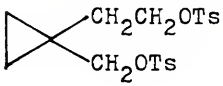
61 62

The ring opening of the cyclopropylcarbinyl system via anionic intermediates has been studied more accurately.[29,30] Roberts and coworker found[29] that the products derived from the Grignard reagent of cyclopropylcarbinyl bromide 63 had the allylcarbinyl structure and determined the reversibility of the rearrangement using ^{14}C or deuterium-labeled allylcarbinyl bromide.



63

As an approach to making 1,1-divinylcyclopropane (22) via the ditosylate 64, we decided to react the ditosylate 28 as a control in the reaction with potassium tert-butoxide in DMSO. We obtained 1-vinylcyclobutene (65) as the major volatile product. This result led us to work on a different approach with the eventual preparation of 22, which we discussed in the previous chapter.



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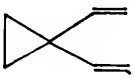

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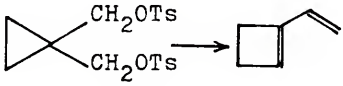


28 65

We became interested in the ring expansion 28→65 mainly for three reasons:

1. 65 was a new compound.
2. 65 contained an extra carbon.
3. To the best of our knowledge the ring expansion was of a type previously unknown.

In this chapter we will consider the preparation and thermal reorganization of 65, mechanistic possibilities that account for the extra carbon and the ring expansion, and studies using simpler cyclopropylcarbinyl derivatives in an attempt to elucidate the mechanism for the ring expansion.

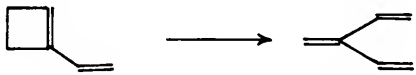
Results and Discussion

Synthesis of 1-Vinylcyclobutene

From the reaction of ditosylate 28 with potassium tert-butoxide in DMSO, 1-vinylcyclobutene 65 was produced in a 10-15% yield as the major volatile component. The nmr spectrum of 65 showed a broad multiplet at δ 2.35-2.70 (4H), doublets at δ 5.05 (J_{df} = 10 cps, 1H) and δ 5.08 (J_{ef} = 17.5 cps, 1H), a broad singlet at δ 5.86 (1H) and doublet of doublets at δ 6.27 (J_{cf} = 10 cps, J_{ef} = 17.5 cps, 1H). The ir spectrum (neat) showed peaks at 3195, 2899, 2817, 1770, 985, 847 and 769 cm^{-1}; the uv had λmax 233 mμ (ϵ 15800); the mass spectrum presented a peak m/e = 80 (P). The structure was confirmed by the reaction of 65 with TCNE to give an adduct whose nmr was similar to that of the adduct of 23 and TCNE.

Thermal Reorganization of 1-Vinylcyclobutene

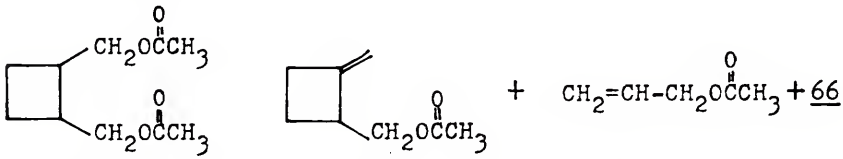
Thermolysis of 1-vinylcyclobutene (65) at 210° for three hours in a small sealed tube produced 2-vinylbutadiene (66) which has been prepared,[31] although by a totally different method. The nmr of 66 in CCl_4 showed a broad multiplet at



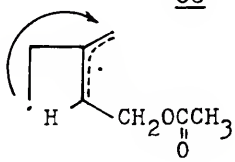
65 66

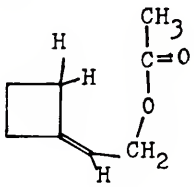
δ 5.10-5.35 combined with a broad singlet at δ 5.54 (6H), doublet of doublets at δ 6.2-6.8 (2H). The ir spectrum (CCl_4) showed peaks at 3077, 2985, 1587, 1418, 1379, 999, 923, 913 and 892 cm^{-1}; the uv had λmax 209 mμ (ϵ 13400), and λ233 mμ (ϵ 9700).

An analysis of the products for the pyrolysis of 1,2-diacetoxymethylcyclobutane (67), at temperatures between 450 and 500°, leads us to think that previous investigators may not have observed the intermediacy of 65 due to the high



67 68



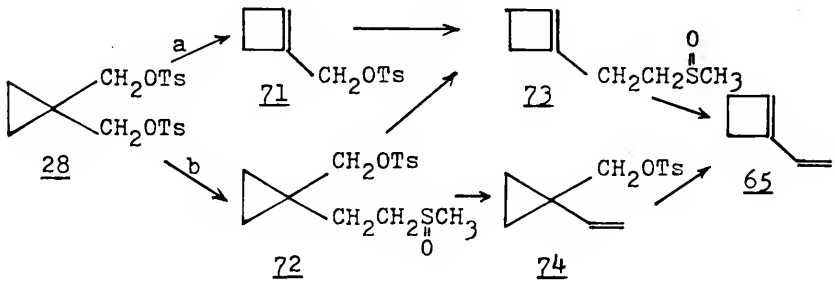


69 70

temperatures used in the pyrolysis of 67. It seems possible that 66 was produced from 68 via 69 and 70, although a less likely eight-membered ring transition state in 68 could also produce 66 directly.

Mechanistic Analysis for the Conversion 28→65

The base-catalyzed elimination of the ditosylate 28 to give 65 could proceed by initial γ-hydrogen abstraction from the cyclopropyl ring to form 71 which would then be attacked by dimsyl anion[32] to produce 73. Base-catalyzed elimination of 73 would generate 65. A variation would be initial attack of dimsyl anion on 28 to form 72 which would either ring expand to 73 or suffer basic elimination to give 74. Base-catalyzed elimination of 74 would also produce 65.



The key point of the various possibilities is that the base-catalyzed ring expansion via 28, 72 or 74 seems to proceed by the novel γ-hydrogen abstraction on the cyclopropyl ring.

The displacement by dimsyl anion of tosylates and bromides, formed from high molecular weight alcohols, has been reported in only two instances.[33] Tosylates and bromides are

known to directly eliminate to produce olefins in the presence of potassium tert-butoxide in DMSO,[34] tosylates favoring elimination and bromides favoring substitution. Similarly the base-catalyzed elimination of the mixed

$$C_nH_{2n+1}CH_2OTs \xrightarrow{\bar{C}H_2\overset{O}{\overset{\|}{S}}CH_3} C_nH_{2n+1}CH_2\overset{O}{\overset{\|}{S}}CH_3 \xrightarrow[DMSO]{\Delta} C_nH_{2n+1}CH{=}CH_2$$

n=12,15

sulfoxide 75 is known to produce isobutene (76).[35] Alkenes are also formed when the mixed sulfoxides are just heated in DMSO.

$$CH_3\text{-}\underset{CH_3}{\overset{H}{C}}\text{-}CH_2\overset{O}{\overset{\|}{S}}CH_3 \xrightarrow[DMSO]{t\text{-}BuOK} CH_3\text{-}\underset{CH_3}{C}{=}CH_2$$

75 76

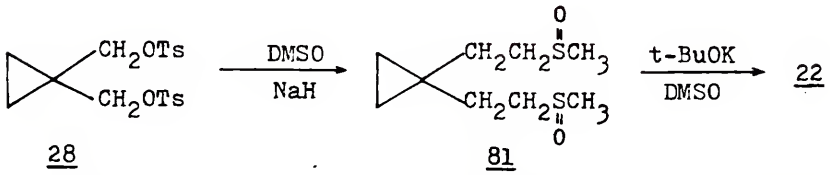
The displacement by dimsyl anion of tosylates, prepared from lower molecular weight alcohols, was further established when we prepared the mixed sulfoxides 77 in 85% and 78 in 71% yields. The mixed sulfoxide 79 was similarly prepared

$$CH_3(CH_2)_4CH_2\overset{O}{\overset{\|}{S}}CH_3 \qquad CH_2CH_2CH_2\overset{O}{\overset{\|}{S}}CH_3 \qquad CH_2CH_2\overset{O}{\overset{\|}{S}}CH_3 \qquad CH_3\overset{CH_3}{\underset{CH_3}{C}}\text{-}CH_2\overset{O}{\overset{\|}{S}}CH_3$$

77 78 79 80

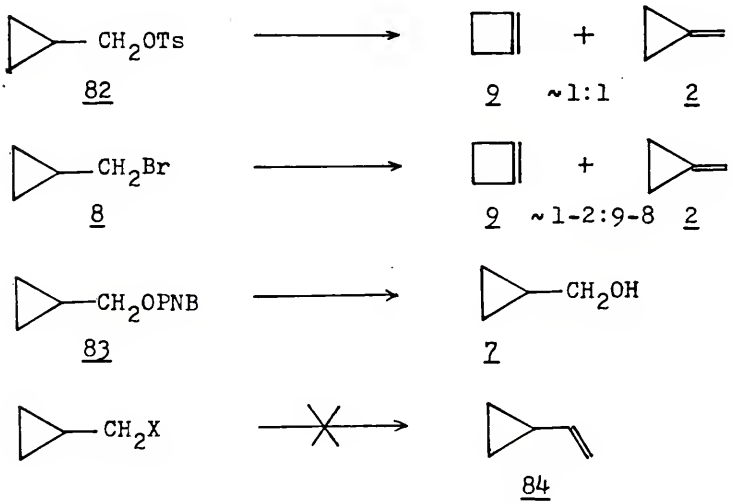
although in a low yield, the reaction being more complex due to the extreme instability of the starting material, benzyl tosylate.[36] We also attempted to prepare 80, and although the reaction proceeded as in previous cases, the apparent high solubility of 80 in water precluded its isolation.

Applying similar conditions for the preparation of olefin via the mixed sulfoxide 81 on the ditosylate 28 resulted in only traces of 22.



Treating 28 with a mixture of sodium hydride in DMSO and potassium tert-butoxide in DMSO produced only 65; no 22 was observed.

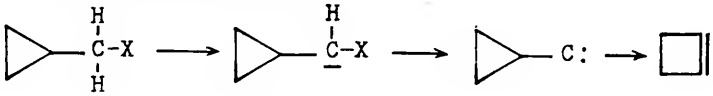
From these results it seems that the tosylate substitution by dimsyl anion is taking place to a lesser degree than is the ring opening under the reaction conditions for the conversion 28→65.



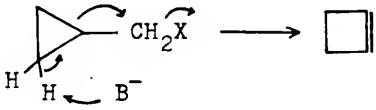
The low yield of 1-vinylcyclobutene (65) and the novelty of the rearrangement led us to work on the simplet parent cyclopropylcarbinyl system. Cyclopropylcarbinyl tosylate (82), cyclopropylcarbinyl bromide (8) and cyclopropylcarbinyl p-nitrobenzoate (83) were prepared[37] and reacted with potassium tert-butoxide in DMSO. The tosylate 82 and the bromide 8 produced cyclobutene (9) and methylenecyclopropane (2) but the p-nitrobenzoate gave only cyclopropylcarbinol (7), a hydrolysis product obtained from the work-up of the nonvolatile portion of the reaction.

Basically two mechanisms could be operating under the reaction conditions for the formation of cyclobutene (9):

a) a carbenoid mechanism.



b) a base-catalyzed γ-hydrogen abstraction in the cyclopropyl ring.



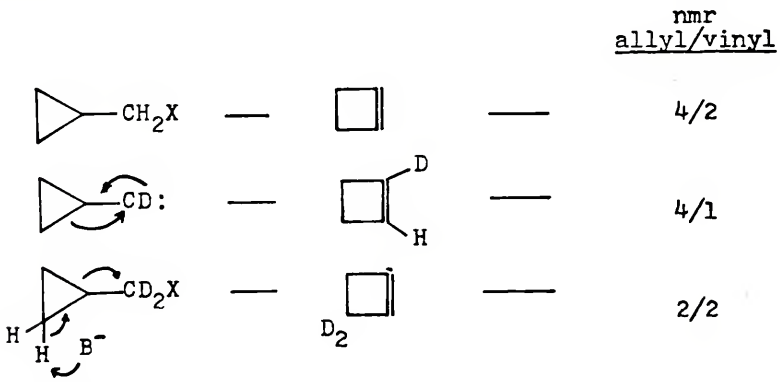
To distinguish between the two possibilities, we prepared the dideuterated tosylate 82-d_2 and the dideuterated bromide 8-d_2. The position of the deuterium in the cyclobutene produced by base-catalyzed elimination should clearly indicate which mechanism is apparently favored.

An allyl/vinyl ratio of ~2/2 was ovserved when both 82-d_2 and 8-d_2 were treated with potassium tert-butoxide in

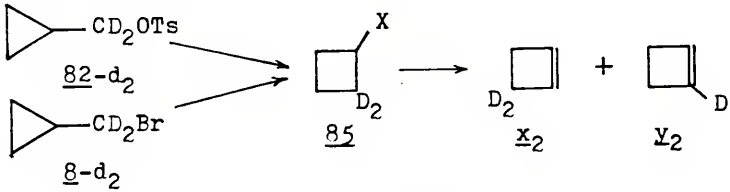
DMSO, thus favoring the base-catalyzed γ-hydrogen abstraction mechanism.

Table VIII

Comparison of allyl/vinyl hydrogen ratios for deuterated and undeuterated cyclobutenes



Another possibility which could affect our proposed mechanism would be a carbonium ring expansion of the tosylates 28, 82 and 82-d_2 and of the bromides 8 and 8-d_2 in DMSO previous to attack by the base. Based on our reaction conditions, we do not favor this explanation. If carbonium ring expansion were to take place, then cyclobutenes x_2 and y_2 would be obtained from the base-catalyzed elimination of the intermediate 85. A primary deuterium isotope effect



k_H/k_D=8 should be observable[38] for the elimination step; since the ratio x_2/y_2 is directly related to k_H/k_D we can

easily calculate the theoretical ratio of allyl/vinyl hydrogens. By solving the algebraic equations a) and b) we obtain the proportions of $\underline{x}_2$ and $\underline{y}_2$, replacing the values obtained for $\underline{x}_2$ and $\underline{y}_2$ in the algebraic equations c) and d). A ratio 1.12 that should be observable by nmr analysis is obtained for the allyl/vinyl hydrogen ratio. This ratio is relatively close to the one observed and proposed in the anionic ring expansion.

a) $x_2 + y_2 = 1$

b) $x_2/y_2 = 8$

$x_2 = 0.889$, $y_2 = 0.111$

c) $x_2 + y_2$ = allyl hydrogens

d) $x_2 + y_2$ = vinyl hydrogens

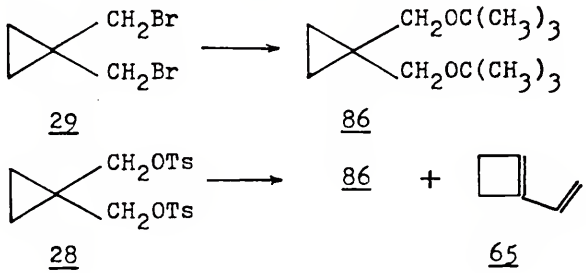
allyl/vinyl = 1.12

Snyder and Soto[39] ruled out the existing possibility of extensive carbonium ion or carbene formation in the reactions of primary alkylbenzenesulfonates with sodium methoxide in DMSO and DMF, reaction conditions that are similar to ours. A third possibility, extensive formation of alkoxydimethylsulfonium cation,[40] $(CH_3)_2SO^+R$, was not ruled out. Although previous studies on the solvolysis of alkylbenzenesulfonates indicated the absence of extensive $(CH_3)_2SO^+R$ formation under the reaction conditions,[41] preferential reaction of alkoxide with a small equilibrium concentration of this cation was not precluded. The possibility of $(CH_3)_2SO^+R$ formation which has been suggested as being responsible for the relative efficiency[40] of olefin formation from many alkyl arenesulfonates in DMSO as a solvent does not modify the key point of our proposed mechanism for the conversion <u>28</u>→<u>65</u>, the base-catalyzed γ-hydrogen abstraction in the cyclopropyl ring.

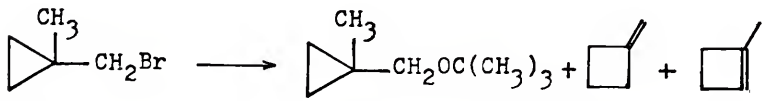
We tested the extent of rearrangement of ditosylate 28 in DMSO, prior to the attack by base, by taking an nmr spectrum of 28 in DMSO-d_6 at room temperature after one hour, reaction time for the conversion 28 → 65. We did not observe any peaks in the spectrum of 28 that could be credited to a cyclobutyl derivative or the intermediacy of $(CH_3)_2SO^+R$. We should mention nevertheless that some rearrangement or decomposition is observed in the nmr spectrum of 28 after ten hours at room temperature; the decomposition is almost complete after thirty-nine hours at room temperature.

We similarly took nmr spectra of the bromide 8-d_2, containing traces of DMF, in DMSO-d_6 and observed no decomposition or rearrangement at all after twelve hours at room temperature; some slight decomposition was nevertheless noticed after one month.

We encountered some limitations to the general use of the ring expansion to cyclobutene derivatives. The dibromide 29 did not produce 65 and only the substitution product 86, which had also been obtained as a nonvolatile by-product for the base-catalyzed reaction of 29, was observed.

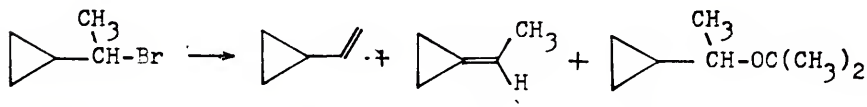


The reaction of 1-methylcyclopropylcarbinyl bromide (87) with potassium tert-butoxide afforded mainly the ether 88; methylenecyclobutane (60) and 1-methylcyclobutene (89) were also present in a 2/1 ratio (20% yield). Competition of primary and secondary hydrogen abstraction by base would give 60 and 89 respectively. We do not favor the possible base-catalyzed isomerization[42] 60 89 since as soon as 60 and 89 are produced they are pumped out of the reaction mixture.



87 88 60 89

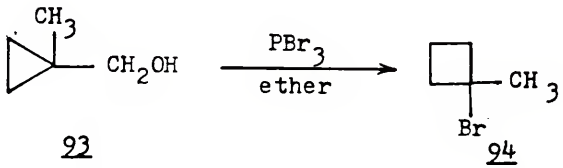
We also prepared the bromide 90 which was subjected to the same basic conditions as 87. The major products of this reaction corresponded to a 2/1 mixture (70% yield) of vinylcyclopropane (84) and ethylidenecyclopropane (91); traces of the corresponding tert-butyl ether 92 were also detected in the volatile fractions collected in the gas traps.



90 84 91 92

Different methods were follwed for the preparation of the bromides 29, 8, 87 and 90. The dibromide 29 was best prepared from the reaction of the corresponding ditosylate 28 and LiBr in refluxing acetone. The bromides 8, 87 and 90 were

best prepared from the reaction of their corresponding alcohols in DMF with triphenyl phosphine and bromine. A previous attempt to prepare 87 from its corresponding alcohol 93 and PBr_3 in ether resulted in the formation of 94.[43]



Conclusion

Our experimental data support the base-catalyzed ring expansion mechanism, via γ-hydrogen abstraction, of the cyclopropylcarbinyl derivatives to the cyclobutene derivatives. Some limitations were encountered in the general applicability of the reaction by a competing substitution process and by competing β and γ-hydrogen abstractions due to the presence of additional methyl groups in the cyclopropylcarbinyl system.

CHAPTER V

EXPERIMENTAL

Melting points were determined on a Thomas-Hoover capillary melting point apparatus. All melting and boiling points are uncorrected. Elemental analyses were performed by Atlantic Microlab, Inc., Atlanta, Georgia. Preparative glpc was performed with a Model A-90-P3 Varian Aerograph gas chromatograph equipped with a Varian Model G2010 ten-inch strip chart recorder. Columns used in glpc are characterized and coded as follows:

DMS-20:	1/4" x 20', 5% dimethyl sulfolane in 60/80 Chromosorb P.
Carbowax-10:	3/8" x 10', 10% Carbowax 1500 on 60/80 Chromosorb P.
Carbowax-13:	3/8" x 13', 10% Carbowax 1500 on 60/80 Chromosorb P.
Carbowax-15:	3/8" x 15', 10% Carbowax 1500 on 60/80 Chromosorb P.
DC-703:	1/4" x 5', 10% Dow Corning Silicone Oil 703 (phenyl methyl) on 60/80 Chromosorb P.

Infrared spectra were recorded on a Perkin-Elmer Model 137. Mass spectra were determined on a Hitachi Model RMU-6E spectrometer. Ultraviolet spectra were recorded on a Cary 15 Recording Spectrophotometer. Nuclear magnetic resonance (nmr) spectra were determined on a Varian A-60 A spectrometer with

compounds dissolved in either CCl_4, acetone-d_6, benzene-d_6 or otherwise specified, with tetramethylsilane (tms) as an internal or external reference. Chemical shifts are given in units of δ.

Cyclopropylcarbinol-d_2 (7-d_2)

The standard reduction procedure,[37c] using $LiAlD_4$, on cyclopropanecarboxylic acid or cyclopropanecarbonyl chloride produced 7-d_2 in 70% and 50% yield, respectively.

bp:	97-98°/250 mm		
ir (NaCl plates):	3333, 2985, 2198, 2083, 1361, 1176, 1099, 971, 909 and 833 cm^{-1}		
nmr (CCl_4):	δ 0.28-0.81	multiplet	4H
	0.90-1.48	multiplet	1H
	4.18	singlet	1H

Cyclopropylcarbinyl Bromide-d_2 (8-d_2)

Two methods were followed for its preparation: a) reaction of the alcohol 7-d_2 with PBr_3 in ether[37c] in ~70% yield, and b) reaction of 7-d_2 with triphenyl phosphine and bromine in DMF, conditions that induce substitution without rearrangement,[44] in ~60% yield.

bp:	62-64°/70 mm		
ir (NaCl plates):	3077, 3012, 2179, 1689, 1429, 1205, 1073, 966 and 833 cm^{-1}		
nmr:	δ 0.25-0.92	multiplet	4H
	1.00-1.50	multiplet	1H

Dideuteriomethylenecyclopropane (2-d_2)

Small-scale reactions were run by mixing 0.01 mol of compound 8-d_2 with 25 ml DMSO immediately before the reaction.

The solution was slowly added over a period of fifteen minutes to a three-necked flask containing a magnetic stirrer and 0.03 mol (excess) of potassium tert-butoxide. The reaction flask, maintained at room temperature, was connected to two liquid nitrogen traps which in turn were attached to a vacuum line (120 mm). Vacuum was applied (20 mm) for an additional forty-five minutes after the addition was completed. Gas chromatographic analysis, using a twenty-foot 5% dimethylsulfolane column in Chromosorb P at 30°, indicated that dideuteriomethylenecyclopropane (2-d_2) was obtained in ~85% yield, along with dideuteriocyclobutene (9-d_2). The retention times for 2-d_2 and 9-d_2 were compared with those of undeuterated methylenecyclopropane and cyclobutene obtained in a similar reaction using undeuterated cyclopropylcarbinyl bromide.

Compound 2-d_2:

ir (gas): 2985, 2941, 2778, 2309, 2212, 2037, 1404, 1109-952, 889, 803-797, 780 and 741-667 cm^{-1}

nmr (CCl_4): δ 1.03 broad singlet

Compound 9-d_2:

ir (gas): 3021, 2899, 2841, 2222, 2165, 1377, 1290, 1143, 862-847, 840 and 725 cm^{-1}

nmr (CCl_4): δ 2.54 singlet 2H
5.97 singlet 2H

gem-Dibromospiropentane-d_2 (3-d_2)

Crude dideuteriomethylenecyclopropane (2-d_2) obtained from the reaction of 17.2 g (0.126 mol) of cyclopropylcarbinyl bromide-d_2 (8-d_2) in 150 ml DMSO and 44 g (0.39 mol) of

potassium tert-butoxide, using a system similar to the one described for the small-scale preparation of 2-d_2, was added without further purification to 800 ml of pentane kept at -75° in a 1000 ml three-necked flask containing 22.4 g (0.2 mol) of potassium tert-butoxide and equipped with a dry ice condenser, a mechanical stirrer and a pressure-equalizing dropping funnel charged with 50.5 g (0.2 mol) of bromoform. The bromoform was slowly added to the reaction mixture over a period of two hours; the temperature of the reaction flask was maintained at -75° for an additional two hours and then gradually increased to room temperature by removing the cooling system (dry ice-acetone). The mixture, dark brown, was poured over 300 ml of ice water, extracted twice with pentane, and the solvent fractions dried over sodium sulfate. The solvent was rapidly removed. Distillation of the residue gave 10 g of compound 3-d_2 bp 73-76°/25 mm (35% yield based on cyclopropylcarbinyl bromide-d_2). A parallel reaction using undeuterated methylenecyclopropane (2) produced undeuterated gem-dibromospiropentane[10a] bp 73-76°/25 mm in 43% yield (based on methylenecyclopropane).

Compound 3-d_2:

bp:	73-76°/25 mm
ir (NaCl plates):	2976, 2198, 1488, 1418, 1122, 1020, 1009, 966, 881, 858 and 729 cm^{-1}
nmr (CCl_4):	δ 1.24 singlet 4H

gem-Dibromospiropentane:[10a]

bp:	73-76°/25 mm (lit.[10a] 63-66°/15 mm)
ir (NaCl plates):	2985, 1493, 1427, 1391, 1086, 1053, 1036, 1018, 904, 897, 851 and 689 cm^{-1}
nmr (CCl_4):	δ 1.24 singlet 4H 1.97 singlet 2H

Vinylidenecyclopropane-d_2 (4-d_2)

A 100 ml three-necked flask was equipped with a magnetic stirrer, a dry nitrogen inlet, a dry ice condenser protected from moisture by an additional dry ice trap and a $CaCl_2$ tube, and a rubber serum cap. In the flask were placed 6.0 g (0.0264 mol) of gem-dibromospiropentane-d_2 (3-d_2) and 5 ml of anhydrous ether. Through the serum cap was slowly injected 14 ml of 4.8% methyllithium (CH_3Li) in ether (0.0305 mol) for twenty minutes. Upon initial addition of the methyllithium, cloudiness due to the immediate formation of lithium bromide was observed. The reaction was followed by gas chromatography using a fifteen-foot SE-30 column at 150°. All of compound 3-d_2 reacted with methyllithium to give almost exclusively compound 4-d_2 along with CH_3Br, a by-product of the reaction. The reaction mixture was stirred for two additional hours then cooled to -10° and 5 ml of water was injected. The layers were quickly separated; the water layer was extracted twice with 10 ml of anhydrous ether. The ether layers were combined, dried over Na_2SO_4 and slowly distilled to remove the bromomethane and most of the ether. The concentrated residue ~10 ml was flash distilled and collected in a small flask cooled with dry ice. An analytical sample of

vinylidenecyclopropane-d_2 (4-d_2) was obtained by gas chromatography using a fifteen-foot SE-30 column at 110°. The amount of highly volatile 4-d_2 recovered was estimated at 1.1 g (60% yield); its retention time was comparable to that of an undeuterated sample of vinylidenecyclopropane (4)[10a] prepared in a parallel reaction.

Compound 4-d_2:

ir (gas): 2976, 2865, 2020, 1031-1015, 985, 971 and 826 cm^{-1}

nmr (CCl_4): δ 1.49 broad singlet

mass spectra: 69 (P), 67, 41, 40 and 39

Compound 4:[10a]

ir (gas): 2976, 2865, 2020, 1449, 1075-1010, 948 and 939 cm^{-1}

nmr (CCl_4): δ 1.49 triplet 4H (J = 3.9 cps)
4.73 quintuplet 2H

mass spectra (m/e): 66 (P), 65, 40 and 39

Dideuteriobiscyclopropylidene (1-d_2)

A modified Simmons-Smith reaction was followed for this step. A 100 ml three-necked flask was equipped with a magnetic stirrer, a dry nitrogen inlet, a sprial reflux condenser protected from moisture by attaching to its top an additional dry ice trap and a $CaCl_2$ tube. The spiral condenser was kept at -78° by continually circulating isopropanol cooled with dry ice. The flask was charged with 7.5 g (0.114 mol) of powdered zinc, 1.23 g (0.114 mol) of cuprous chloride and 10 ml of anhydrous ether. The mixture was refluxed for thirty minutes and then cooled to room temperature before slowly

adding ~10 ml of ether solution containing 4-d_2 and 2.34 ml (0.0288 mol) of diiodomethane. Over a period of three days and two nights the mixture was refluxed, for a total of thirty-four daytime hours, and maintained overnight at room temperature for a total of twenty hours. The contents of the reaction mixture were poured into 50 ml of ice water containing 5% HCl and left to achieve complete hydrolysis for forty-five minutes. The solution was quickly filtered; the organic layer was separated, washed with 50 ml of 5% sodium thiosulfate and 50 ml of water and then dried over Na_2SO_4. The ether solution was flash distilled and the volatile products collected in a flask cooled in dry ice. Gas chromatography using a five-foot DC-703 column at 90° indicated that compound 4-d_2 was still partially unreacted and that new products were formed which were identified as dideuteriomethylenespiropentane (6-d_2), dispiro (2.1.2.0) heptane -d_2 (5-d_2) and dideuteriobiscyclopropylidene (1-d_2), in an approximate ratio of 1:2:2, by the similarity of retention times to those of authentic undeuterated samples prepared in a parallel reaction. Small traces of at least two unidentified products were also found. The retention times were, in order: CH_3Br < ether < 4 < 6 < benzene ≤ 5 < 1. Approximately 0.15 g

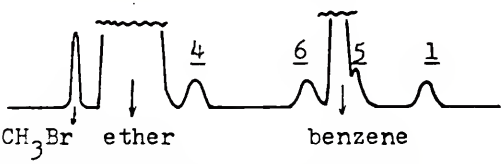


Figure 2. Gas chromatographic retention time comparison for compounds 1, 4, 5 and 6.

of pure dideuteriobiscyclopropylidene (1-d_2) (11.3% yield) was collected by gas chromatography.

Compound 1-d_2:

ir (gas):	3077, 2985, 2326, 2222-1613, 1266-1250, 1087-1047, 980, 968, 870-855, 787 and 781-766 cm^{-1}
nmr (C_6D_6):	δ 1.25 broad singlet
mass spectra (m/e):	82 (P), 81, 80, 67, 66, 65, 54 and 52

Compound 5-d_2:

nmr (CCl_4):	δ 0.57	multiplet	3H	symmetrical
	0.78	multiplet	3H	
	1.14	singlet		
mass spectra (m/e):	96 (P)			

Thermolysis of Dideuteriobiscyclopropylidene (1-d_2)

Three independent samples were prepared, two using C_6D_6 as solvent and one using pentane. A general method for the thermolysis consisted of transferring via vacuum line 0.025 g of 1-d_2 to a 200 ml glass pyrolysis tube. Deuterated benzene or pentane, 0.3 ml, was similarly transferred via vacuum line to the glass pyrolysis tube. The pyrolysis tube was degassed, sealed under vacuum, wrapped with glass wool and heated in a furnace tube at 214° for forty-nine hours. After pyrolysis the narrow part of the pyrolysis tube was chilled at -190° to condense the sample. This part was quickly cut while cold. An nmr, when C_6D_6 was the solvent, indicated no dimer formed during the thermolysis. The sample was dried by passing it through $MgSO_4$ via vacuum line. Traces of dispiro (2.1.2.0)

heptane-d_2 (5-d_2) present in the original sample were removed after the pyrolysis by gas chromatography using a five-foot DC-703 column at 90°. A pure sample containing deuterated methylenespiropentanes x, y and z was obtained and analyzed by nmr (see Table II).

2,2-Dibromomethylenecyclopropane (10)

A 1000 ml three-necked flask was equipped with a mechanical stirrer, a dry ice condenser and a pressure-equalizing dropping funnel and protected from moisture by attaching an additional dry ice trap to its top and a $CaCl_2$ tube. The flask, charged with 800 ml of dried pentane and 22.4 g (0.187 mol) of potassium tert-butoxide, was cooled to -75° with a dry ice-acetone bath. Slowly 65 g (1.63 mol) of allene was condensed in the pentane, and 38 g (0.15 mol) of bromoform contained in the funnel was added to the pentane solution over a period of four hours. The reaction mixture turned light yellow upon initial addition of the bromoform and deep brown at the end of the addition. The reaction flask was allowed to reach room temperature by removing the dry ice-acetone bath. The contents of the dark reaction mixture were poured into 600 ml of ice water; the layers quickly separated. The water layer was extracted with 300 ml of pentane. The combined organic layers were dried over $MgSO_4$ and the solvent quickly evaporated using a rotor water vacuum evaporator. Approximately 15 g of dark residue remained. An nmr of this residue showed peaks corresponding to 10 and $CHBr_3$ in a ratio of 1/5.2, along with some other peaks. Flash

distillation of the crude product produced 11 g showing nmr peaks corresponding to 10 and $CHBr_3$ (in a ratio of 1/7.5). The yield of 10 was calculated as ~5% from the initial amount of bromoform used for the reaction. An nmr of fractions from an attempted slow distillation of 10 indicated the presence of a new peak. When samples containing 11 were injected into a thirteen-foot Carbowax column at 160° the proportion of 10 decreased and that of the new peak increased (ratio 1/4.5). The collected new peak showed spectral characteristics for dibromomethylenecyclopropane (11). The nmr of both 10 and 11 were similar to the dichloro analogs.[45]

Compound 10:

nmr (CCl_4):	δ 2.27	triplet	2H	(J = 2.4 cps)
	5.63	multiplet	1H	(symmetrical)
	6.04	multiplet	1H	

Compound 10 + 11:

ir (NaCl plates): 2941, 1692, 1634, 1460-1391, 1198, 1149, 1042, 1022, 911, 749, 722 and 697 cm^{-1}

Compound 11:

ir (NaCl plates): 2941, 1692, 1634, 1449, 1372, 1096, 1042, 1022, 911, 735, 722 and 697 cm^{-1}

nmr (CCl_4): δ 1.40 singlet

2,2-Bisbromomethyl-1,3-propanediol (25)

This compound was prepared by the improved method of M. Saucier and coworkers.[46]

mp: 109-110°

Cyclopropane-1,1-dicarbinol (27)

This compound was prepared by the method of B. Chamboux and coworkers,[47] and by lithium aluminum hydride reduction of diethyl cyclopropane-1,1-dicarboxylate 26.[48]

bp: 121°/12 mm

ir (NaCl plates): 3322, 2857, 1429, 1212, 1053-990, 917 and 870 cm^{-1}

nmr ($CD_3\overset{O}{\overset{\|}{C}}CD_3$): δ 0.40 singlet 4H
3.52 doublet 4H
4.06 triplet 2H

Cyclopropane-1,1-dicarbinol Di-p-toluenesulfonate (28)

The method of B. Chamboux and coworkers[49] was used for the preparation of this compound.

mp: 114°

ir (KBr): 2985, 1942, 1818, 1786, 1667, 1600, 1361, 1326, 1183, 1098, 1047, 1010, 940, 855-838 and 759 cm^{-1}

nmr ($CD_3\overset{O}{\overset{\|}{C}}CD_3$): δ 0.63 singlet 4H
2.45 singlet 6H
3.93 singlet 1H
7.44 doublet 2H (J = 8 cps) (symmetrical)
7.77 doublet 2H (J = 8 cps)

Cyclopropane-1,1-dicarbinyl Dibromide (29)

Dry acetone was distilled from potassium permanganate and anhydrous potassium carbonate; 42.7 g (0.104 mol) of cyclopropane-1,1-dicarbinol di-p-toluenesulfonate and 50.5 g (0.58 mol) of lithium bromide were refluxed in 300 ml of this acetone, protected from moisture. A magnetic stirrer prevented serious bumping. After the reaction was completed the

the acetone was removed on a rotary evaporator and the residual oil was taken up in ether. The ether material was washed well with water and brine and dried over anhydrous potassium carbonate. Distillation afforded 20 g (84% yield) of a colorless liquid that was best stored over anhydrous potassium carbonate.

bp:	91-93°/19 mm (lit.[50] 82-87°/20 mm)
ir (NaCl plates):	3049, 2976, 1429, 1325, 1227, 1054, 1022, 970, 961, 943, 883 and 830 cm^{-1}
nmr (CCl_4):	δ 0.9 singlet 4H 3.45 singlet 4H

Cyclopropane-1,1-diacetonitrile (30)

Two methods were followed to prepare this compound.

Method 1: The method of Chamboux and coworkers was followed.[49]

Method 2: To a 2000 ml three-necked flask equipped with a pressure-equalizing dropping funnel, a reflux condenser and a mechanical stirrer were added 400 ml of DMSO dried over NaH and 220 g (3.4 mol) of potassium cyanide. The system was heated to 70°. Slowly 83.6 g (0.366 mol) of cyclopropane-1,1-dicarbinyl dibromide dissolved in 200 ml of dried DMSO was added. During the addition the temperature was maintained at around 80°. Once the addition was completed the system was heated to 100° and kept at that temperature for twenty-one hours. The cooled solution was filtered and the precipitate (potassium bromide) was washed with ether. The filtrate was treated with water and extracted with ether. The combined ether extracts were dried with sodium sulfate. Fractional distillation gave 32 g (73% yield) of a colorless liquid.

bp: 100-119°/0.6-0.8 mm (lit.[49] 140°/11 mm)

ir (NaCl plates): 2950, 2262, 1420 and 1031 cm^{-1}

nmr (CCl_4): δ 0.77 singlet 4H
2.53 singlet 4H

Cyclopropane-1,1-diacetic Acid (31)

This compound was prepared by the method of B. Chamboux and coworkers.[15]

bp: 87°

ir (KBr): 3333, 2778, 2632, 1724-1695, 1408, 1316-1176, 1060, 1029, 971-905, 889, 791 and 708 cm^{-1}

nmr ($CD_3\overset{O}{\overset{\|}{C}}CD_3$): δ 0.53 singlet 4H
2.42 singlet 4H
5.9-6.9 broad singlet 1H

Cyclopropane-1,1-diethanol (32)

Cyclopropane-1,1-diacetic acid was reduced by the standard method using lithium aluminum hydride[37c] in 80% yield.

mp: 68-70°

ir (KBr): 3390, 2907, 1481, 1447, 1427, 1366, 1058, 1028, 1015, 960, 909 and 865 cm^{-1}

nmr ($CD_3\overset{O}{\overset{\|}{C}}CD_3$): δ 0.28 singlet 4H
1.51 triplet 4H (J = 7 cps)
3.65 triplet 4H (J = 7 cps)
3.3-3.8 broad singlet 2H

Cyclopropane-1,1-diethanol Di-p-toluenesulfonate (33)

In a 250 ml three-necked flask equipped with a mechanical stirrer and an ice-salt bath to keep the temperature of the flask between 0 and -10° were placed 9 g (0.069 mol) of cyclopropane-1,1-diethanol and 30.2 g of dry pyridine: 36.6 g

(0.38 mol) of p-toluenesulfonyl chloride was added in small portions. The reaction mixture was stirred at 0° for one-half hour and then for another hour letting the system slowly reach room temperature. The slurry formed was poured over 200 ml of ice water; the precipitate formed was quickly filtered. Vacuum was applied overnight and the crude tosylate 29 g mp $54\text{-}57^{o}$ was used for the next reaction.

mp:	$54\text{-}57^{o}$			
ir (KBr):	2985, 2924, 1942, 1802, 1667, 1600, 1471, 1429, 1350, 1198, 1176, 1110, 1058, 1021, 998, 935, 885, 855, 820 and 775 cm^{-1}			
nmr ($CD_3\overset{O}{\overset{\|}{C}}CD_3$):	δ 0.26	singlet	4H	
	1.55	triplet	4H	(J = 7 cps)
	2.42	singlet	6H	
	4.1	triplet	4H	(J = 7 cps)
	7.42	doublet	4H	(J = 8 cps) (symmetrical)
	7.78	doublet	4H	(J = 8 cps)

1,1-Divinylcyclopropane (22)

A 500 ml dried three-necked flask was equipped with a micro-distillation head, a pressure-equalizing dropping funnel, a bent tube sealed on one end and a magnetic stirrer. To the flask were added 2.6 g (0.02 mol) of cyclopropane-1,1-diethanol di-p-toluenesulfonate and 30 ml of dried DMSO. The sealed tube was charged with 5.6 g (0.05 mol) of potassium tert-butoxide and the pressure-equalizing funnel charged with 50 ml of DMSO. The reaction flask was kept at room temperature during the reaction. Vacuum was applied (50 mm) while the potassium tert-butoxide was added in small portions

during fifteen minutes. The reaction mixture changed color, from green to brown. The remaining DMSO was added and 50 mm of vacuum was applied for fifteen more minutes. Full vacuum was then applied for one hour. The volatile compounds collected in the gas traps were degassed and transferred to a small tube that was sealed and kept in the refrigerator until separation was accomplished using a fifteen-foot Carbowax column.

ir (NaCl plates):	3058, 2967, 1639, 1427, 991, 951, 917, 902 and 863 cm^{-1}		
nmr (CCl_4):	δ 0.79	singlet	4H
	4.89	doublets (J_{bd} = 9.5, J_{bc} = 1.7 cps)	2H
	4.91	doublets (J_{cd} = 18, J_{bc} = 1.7 cps)	2H
	5.78	doublets (J_{bd} = 9.5, J_{cd} = 18 cps)	2H
mass spectra:	94 (P), 79 (base), 77 and 39		
elemental anal. for C_7H_{10}:	calc.	H: 10.71	C: 89.29
	found	H: 10.88	C: 89.12

Thermolysis of 1,1-Divinylcyclopropane (22)

Compound 23, 1-vinylcyclopentene,[18] was smoothly obtained when 1,1-divinylcyclopropane 22 was thermolyzed. The general method used is described below: 0.030 g of compound 22 was transferred to a 900 ml pyrolysis tube via vacuum line. Pentane or benzene, 0.3 ml, was similarly transferred via vacuum line to the pyrolysis tube. The sample was degassed and sealed under full vacuum. The pyrolysis tube

was covered with glass wool and heated in a tube furnace at 285° for twenty hours. The temperature of the furnace was lowered and when it reached 100° the tube was removed. The narrow part of the pyrolysis tube was chilled at -190° to condense the sample and quickly cut while cold. The pyrolysis product was separated by gas chromatography using a ten-foot Carbowax column at 80°. To the collected sample 0.3 ml of CCl_4 was added to take an nmr. If traces of water were present after the nmr was taken, they were eliminated by passing the solution through anhydrous $MgSO_4$ via vacuum line. Yields were ~90%.

Compound 23:

ir (NaCl plates):	2924, 2825, 1639, 1587, 990, 902 and 818 cm^{-1}		
nmr (CCl_4):	δ 1.93	broad doublet	2H
	2.30-2.50	broad multiplet	4H
	4.94	doublets (J_{dg} - 9.5, J_{de} = 2 cps)	1H
	4.96	doublets (J_{eg} = 18, J_{de} = 2 cps)	1H
	5.62	broad singlet	1H
	6.48	doublet of doublets (J_{dg} = 9.5, J_{eg} = 18 cps)	1H
uv:	λmax 233 mμ (ϵ 22,400), λ 240 mμ (ϵ 16,650), λ 227 mμ (ϵ 21,111) and λ202 mμ (ϵ 12,200)		
mass spectra (m/e):	94 (P)		
elemental anal. for C_7H_{10}:	calc. H: 10.71	C: 89.29	
	found H: 10.88	C: 89.14	

Reaction of 1-Vinylcyclopentene (23) with TCNE

Small portions of tetracyanoethylene (TCNE) were slowly added to an nmr tube containing 0.03 g of compound 23 in C_6D_6. The nmr peaks corresponding to 23 disappeared and those corresponding to the Diels-Adler adduct appeared. The solvent C_6D_6 was quickly evaporated and an ir of the crude product was taken.

ir (NaCl plates): 2778, 2174, 1399, 1235 and 850 cm^{-1}

nmr (C_6D_6): δ 0.9-2.9 multiplets 9H
4.5-4.7 multiplet 1H

Rate Constant for Compound 22

A standard sample was prepared by condensing via vacuum line in a 10 ml tube 3 ml of benzene (to be used as solvent), 0.03 g of 1,1-divinylcyclopropane and 0.03 g of n-heptane (to be used as internal standard). The homogenized content of the 10 ml tube was divided into six portions, each placed in a 3 ml tube and sealed at atmospheric pressure. The tubes were heated in a well-insulated, well-stirred bath containing GE-SF-1093 (100) silicone fluid. This oil did not decompose even at the highest temperature used in our study. The bath was heated by one 500-W bar heater to a temperature 10° below that desired. A smaller 100-W coiled-wire heater enclosed in glass tubing was used in conjunction with a Hallikainen platinum resistance thermometer (model 1146) and a Hallikainen Resistotrol temperature regulator, off-on type, to bring the temperature to the desired value and to maintain it there. Temperatures were monitored using a calibrated

iron-constantan thermocouple in conjunction with a Honeywell Model 2702 potentiometer. Each tube was withdrawn from the bath at an appropriate time, cooled in dry ice, opened, and the contents analyzed by gas chromatography using a ten-foot Carbowax column at 80°. The gas chromatograph was attached to an Infotronics Digital Readout System Model CRS-100 to facilitate and minimize the error in the determination of the peak areas. Each tube's gas chromatographic result constituted a single point in determining a rate constant. Rate constants at three different temperatures were obtained (see Table III).

Temp(°C)	Temp(°K)	10^{-3}/Temp(°K)	k(10^{-5})sec^{-1}
233.5	506.5	1.9743	3.148
242.0	515.0	1.9417	6.023
257.0	530.0	1.8868	18.342

Cyclopropane-1,1-diethanol-d_4 (32-d_4)

The standard method of reduction,[51] using $LiAlD_4$, produced 32-d_4 in ~80% yield.

nmr ($CD_3\overset{O}{\overset{\|}{C}}CD_3$): δ 0.28 singlet 4H
1.51 broad singlet 4H
3.4 broad singlet 2H

Cyclopropane-1,1-diethanol-d_4 Di-p-toluenesulfonate (33-d_4)

The method used for the preparation of compound 33 was followed for the preparation of 33-d_4. The crude ditosylate was used in the elimination step without further purification.

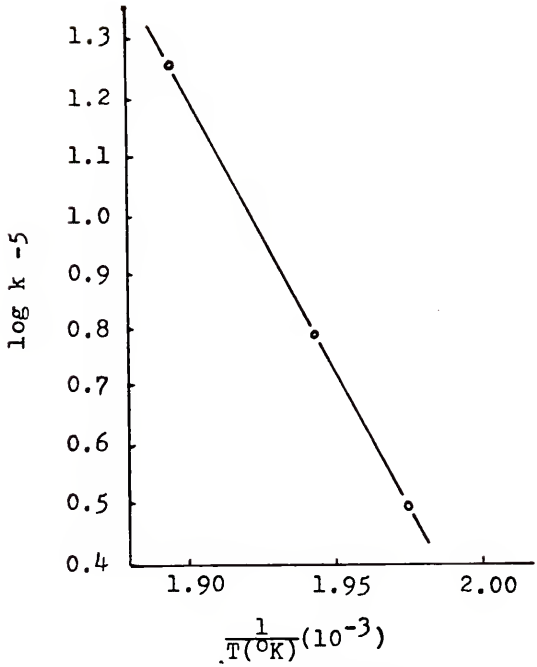


Figure 3. Arrhenius plot for the reaction 22 → 23.

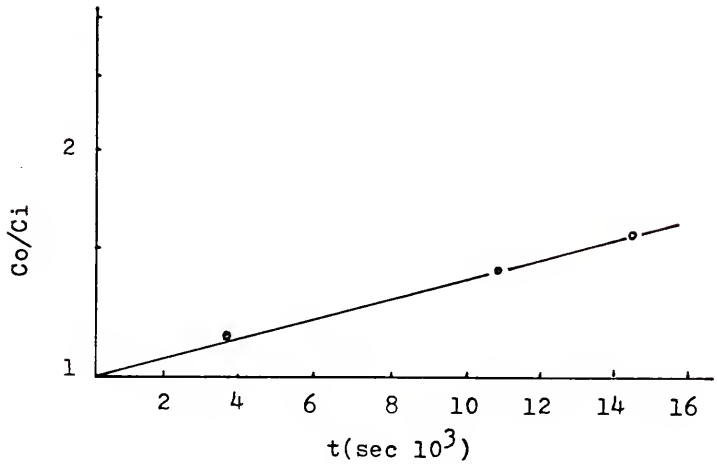


Figure 4. Concentration vs. time plot for the reaction 22 → 23 at 233.5°.

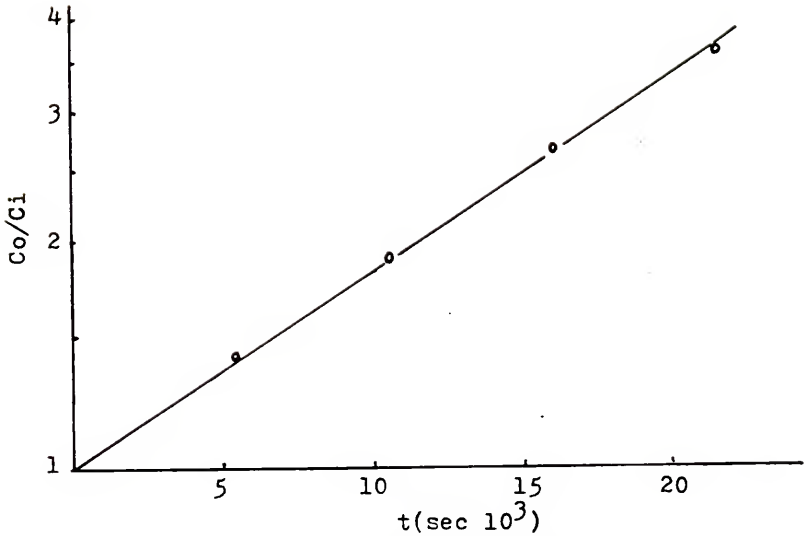


Figure 5. Concentration vs. time plot for the reaction 22→23 at 242°.

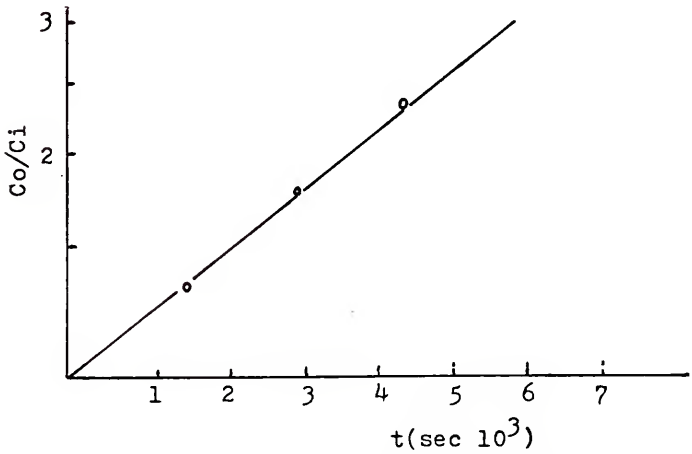


Figure 6. Concentration vs. time plot for the reaction 22→23 at 257°.

1,1-Divinylcyclopropane-d_4 (22-d_4)

The same procedure used in the preparation of 22 from 33 was followed to prepare 22-d_4 from 33-d_4.

ir (gas): 2967, 2326, 2222, 1590, 1010, 952-893 and 746-709 cm^{-1}

nmr (CCl_4): δ 0.79 singlet 4H
5.74 broad multiplet 2H

Cyclopropane-1,1-diacetic Anhydride (34)

This compound was prepared by refluxing 19 g (0.12 mol) of cyclopropane-1,1-diacetic acid (31)[15] with 30 g (0.38 mol) of acetyl chloride for two hours. After the reaction was completed the excess of acetyl chloride was mostly distilled off. Then full vacuum was applied to eliminate last traces of acetyl chloride. The paste that remained in the reaction pot was utilized in the next step without further purification.

Cyclopropane-1-acetic Acid, 1-Ethyl Acetate (35)

To compound 34 was added 10 ml of absolute ethanol and the mixture was refluxed for one and one-half hours. Fractional distillation gave 17.6 g of compound 35 (73.5% yield) based on compound 31.

bp: 131-133°/ 0.4 mm

ir (NaCl plates): 3175, 3049, 2950, 2632, 1980, 1739-1709, 1408, 1370, 1307, 1253-1143, 1036, 966 and 935 cm^{-1}

nmr (CCl_4):	δ 0.54	singlet	4H
	1.26	triplet	3H (J = 7 cps)
	2.36	singlet	2H
	2.46	singlet	2H
	4.02	quartet	2H (J = 7 cps)
	11.56	singlet	1H

Cyclopropane-1-acetylchloride, 1-Ethyl Acetate (36)

To a 250 ml round-bottomed flask with an attached condenser was added 17.6 g (0.095 mol) of compound 47. The flask was ice water cooled while adding slowly 27 g (ρ = 1.65) (0.226 mol) of thionyl chloride. The mixture was refluxed for two hours, then cooled and finally fractionally distilled. A total of 17.4 g (90% yield) of compound 36 was obtained.

bp: $95^{o}/0.45$ mm

ir (NaCl plates): 3058, 2959, 2933, 1812, 1739, 1399, 1374, 1314, 1250, 1205-0043, 1099, 1064, 1036, 1005, 962, 943, 909, 866, 784, 746 and 697 cm^{-1}

nmr (CCl_4):	δ 0.58	singlet	4H
	1.26	triplet	3H (J = 7 cps)
	2.32	singlet	2H
	3.03	singlet	2H
	4.11	quartet	2H (J = 7 cps)

Cyclopropane-1-ethanol, 1-Ethyl Acetate (37)

To a well-stirred solution of 16.2 g (0.43 mol) of $NaBH_4$ in 70 ml of anhydrous dioxane was added a solution of 17.4 g (0.85 mol) of compound 36 in 25 ml of anhydrous dioxane over a period of forty-five minutes. After refluxing the mixture for five hours it was cooled and slowly and carefully poured over 600 ml of ice water and extracted with six 200 ml

portions of ether. After extraction, the aqueous layer was acidified with HCl to pH 4 and again extracted with four more 200 ml portions of ether. The ether extracts were combined and dried over sodium sulfate. After removal of the ether the reaction product was fractionally distilled, giving 6.2 g (42% yield) of the expected product.

bp: 95-97°/ 0.2 mm or 106-108°/1.75 mm

ir (NaCl plates): 3448, 2941, 2899, 1727, 1460-1366, 1307, 1250, 1176-1143, 1093, 1053, 1036, 981 and 952 cm^{-1}

nmr (CCl_4):

δ 0.42	singlet	4H
1.25	triplet	3H (J = 7 cps)
1.63	triplet	2H (J = 6 cps)
2.23	singlet	2H
2.72	broad singlet	1H
3.62	triplet	2H (J = 6 cps)
4.11	quartet	2H (J = 7 cps)

Cyclopropane-1,1-diethanol-d_2 (38)

This compound was prepared by the standard method of reduction,[51] treating compound 37 with $LiAlD_4$ in ~80% yield.

ir (KBr): 3448, 3279, 2899, 2841, 2183, 2092, 1473, 1445, 1422, 1348, 1130, 1099, 1055, 1032, 1010, 960, 881 and 810 cm^{-1}

nmr ($CD_3\overset{O}{\overset{\|}{C}}CD_3$):

δ 0.28	singlet	4H
1.51	triplet	2H (J = 7 cps)
1.51	broad singlet	2H
3.33	broad singlet	2H
3.65	triplet	2H (J = 7 cps)

Cyclopropane-1,1-diethanol-d_2 Di-p-toluenesulfonate (39)

The preparation of this compound was similar to that of

33. The crude ditosylate was used without further purification in the preparation of 22-d_2.

1,1-Divinylcyclopropane-d_2 (22-d_2)

The same procedure used in the preparation of 22 from 33 was followed in the preparation of 22-d_2 from 39.

ir (gas): 3058, 2967, 2326, 1639, 1590, 1427, 991, 952-893, 763 and 725 cm^{-1}

nmr (CCl_4):	δ 0.79	singlet	1H
	4.89	doublets	1H
	4.91	doublets	1H
	5.74	broad multiplet	1H
	5.78	doublet of doublets	

Thermolysis of 1,1-Divinylcyclopropane-d_2 (22-d_2), Intramolecular Isotope Effect

Five independent samples were prepared. The experimental procedure was similar to the one followed for the thermolysis of 22. Traces of water present in collected samples containing x_1 and y_1 were eliminated by treating the samples with powdered $MgSO_4$ via vacuum line. Nmr analysis afforded the ratio of vinyl hydrogens f/de and g/de in the mixture of x_1 and y_1 (see Table IV, p. 21).

ir (NaCl plates): 2924, 2825, 2174, 2088, 1639, 1587, 1546, 990, 943, 902, 820-763 and 722 cm^{-1}

Thermolysis of 22 and 22-d_4, Intermolecular Isotope Effect

The intermolecular isotope effect k_H/k_D is directly related to the ratio of the rate constants of compounds 22 and 22-d_4. The preparation of the samples and kinetic procedure were similar to those followed for the determination

of rate constants for compound 22. For the intermolecular isotope effect compounds 22 and 22-d_4 were run simultaneously at 242°. An intermolecular isotope effect k_H/k_D = 1.08±0.07 was obtained. The ratio of the rate constants of 22 and 22-d_4 for each point of the kinetic plot was determined.

Point	k_H/k_D	Point	k_H/k_D
1	0.9753	4	1.1011
2	1.0844	5	1.1557
3	1.0762	Average:	1.08±0.07

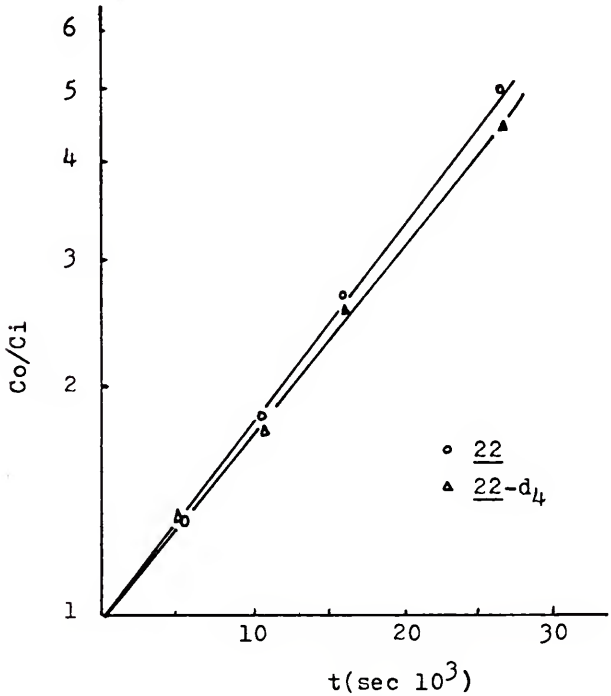


Figure 7. Concentration vs. time plot comparison for compounds 22 and 22-d_4.

3-Methylenecyclobutanecarbonitrile (40)

This compound was prepared by the method of Caserio and coworkers[51] from allene and acrylonitrile in a 1.5 liter stainless steel Parr bomb. Toluene was used as a solvent and traces of hydroquinone were added to prevent dimerization of allene.

bp:	74-76°/31 mm		
ir (NaCl plates):	2967, 2924, 2874, 2237, 1686, 1664, 1408 and 889 cm^{-1}		
nmr (CCl_4):	δ 3.08	multiplet	5H
	4.87	multiplet	2H

3-Methylenecyclobutanecarboxylic Acid (41)

The method of Caserio and coworkers[51] was used in preparing this compound.

bp:	106-108°/8 mm (lit.[51] 99-101°/9 mm)		
ir (NaCl plates):	2941, 2667, 3236, 1709, 1418, 1333, 1290, 1212, 939 and 881 cm^{-1}		
nmr (neat):	δ 3.00	multiplet	5H
	4.80	multiplet	2H
	12.10	singlet	1H

3-Methylenecyclobutanecarbinol (42)

This compound was prepared following the standard method of reduction,[51] with $LiAlH_4$, in ~80% yield.

bp:	101-103°/78 mm		
ir (NaCl plates):	3279, 2899, 1669, 1408, 1044, 1020, 971 and 877 cm^{-1}		
nmr ($CD_3\overset{O}{\overset{\|\|}{C}}CD_3$):	δ 2.52	broad multiplet	5H
	3.50-3.60	broad doublet	3H (2+1)
	4.69	multiplet	2H

3-Methylenecyclobutylcarbinyl Tosylate (43)

A 1000 ml three-necked flask was equipped with a mechanical stirrer, an ice-salt bath to maintain the temperature between 0 and -10°, and was charged with 33 g (0.338 mol) of 3-methylenecyclobutanecarbinol (42) and 67.5 g of dry pyridine. A positive pressure of nitrogen was maintained at all times and the flask was protected from moisture. In small portions, 81 g (0.424 mol) of p-toluenesulfonyl chloride was added with vigorous stirring over a period of forty-five minutes. The reaction mixture was stirred at ~0° for one-half hour and then allowed to reach room temperature. The contents of the reaction flask were poured over 300 ml of ice water with vigorous stirring. A precipitate formed and was quickly filtered. The dried, crude 80.5 g of tosylate (95% yield) was used for the next reaction.

mp: 42-44°

nmr ($CD_3\overset{O}{\overset{\|}{C}}CD_3$):	δ 2.1-2.9	broad multiplet	5H
	2.45	singlet	3H
	4.10	broad multiplet	2H
	4.71	multiplet	2H
	7.45	doublet	2H (J = 8 cps)
	7.81	doublet	2H (J = 8 cps)

3-Methylenecyclobutaneacetonitrile (44)

To a 500 ml three-necked flask equipped with a pressure-equalizing dropping funnel, a reflux condenser, a thermometer and a mechanical stirrer, were added 51.5 g (0.79 mol) of potassium cyanide and 100 ml of DMSO. The mixture was gently heated to 70°. The dropping funnel was charged with a

suspension of 40 g (0.16 mol) in 50 ml of DMSO and the suspension was slowly added to the reaction flask so that the temperature was below 80° during the addition. After the addition was completed the reaction was heated over a period of fifteen hours at 90°. The system was cooled down and filtered; water was added to the filtrate, and a small organic layer formed on top. The lower aqueous layer was extracted with ether. All the fractions containing 3-methylenecyclobutaneacetonitrile were mixed and dried over $MgSO_4$. Distillation afforded 15.5 g of the product (91.3% yield).

bp:	102-104°/54 mm		
ir (NaCl plates):	2941, 2899, 2247, 1678, 1416, 1062 and 883 cm^{-1}.		
nmr (CCl_4):	δ 2.48	doublet	2H
	2.2-3.1	broad multiplet	5H
	4.79	multiplet	2H

3-Methylenecyclobutaneacetic Acid (45)

To a solution of 82 g (1.26 mol) of 86% potassium hydroxide pellets in 450 ml of 50% aqueous ethanol was added 28.7 g (0.268 mol) of 3-methylenecyclobutaneacetonitrile (44). The misture was heated on a steam bath; after about three hours the ammonia evolution had ceased and the solvent was evaporated under water aspirator vacuum. The residual solid was dissolved in 100 ml of water and evaporated again to eliminate completely traces of ethanol. About 100 ml of water was again added and concentrated hydrochloric acid was slowly added until the solution became acid to Congo red. Two layers were formed; the lower aqueous layer was extracted with four

portions of 100 ml of ether. The top layer was mixed with the ether extracts and dried over anhydrous magnesium sulfate. Fractional distillation afforded 27.8 g of the product (~82% yield).

bp:	$132^{o}/23$ mm		
ir (NaCl plates):	3058, 2899, 2632, 1709, 1408, 1307, 1212, 943 and 881 cm^{-1}		
nmr (CCl_4):	δ 2.54	doublet	2H
	2.2-3.2	broad multiplet	5H
	4.72	multiplet	2H
	11.64	singlet	1H

3-Methylenecyclobutane Ethanol (46)

This compound was prepared following the standard method of reduction,[51] with $LiAlH_4$, in 91% yield.

bp:	$95-96^{o}/23$ mm		
ir (NaCl plates):	3333, 3049, 2915, 1678, 1410, 1060 and 877 cm^{-1}		
nmr ($CD_3\overset{O}{\overset{\|\|}{C}}CD_3$):	δ 1.73	broad quartet	2H
	2.1-2.9	broad multiplet	5H
	3.53	broad triplet	3H (2+1)
	4.70	multiplet	2H
nmr ($CDCL_3$):	δ 1.73	broad quartet	2H
	2.1-3.0	broad multiplet	6H (5+1)
	3.65	broad multiplet	2H
	4.73	multiplet	2H

Tosylate of 3-Methylenecyclobutane Ethanol (47)

The same method followed for the preparation of 3-methylenecyclobutanecarbinyl tosylate (43) was used in preparing this compound. Tosylate 47 was obtained in ~98% yield as an

oily compound which without further purification was used in the next step.

ir (NaCl plates): 3030, 2933, 1678, 1600, 1493, 1353, 1190, 1178, 1099, 990, 948, 877, 820 and 775 cm^{-1}

nmr ($CD_3\overset{O}{\overset{\|}{C}}CD_3$):

δ 1.78	broad quartet	2H
2.1-2.9	broad multiplet	5H
2.40	singlet	3H
4.01	triplet	2H
4.67	multiplet	2H
7.42	doublet	2H
7.80	doublet	2H

3-Vinylmethylenecyclobutane (48)

A 300 ml three-necked flask was equipped with a micro-distillation head connected to two gas traps kept in liquid nitrogen and a pressure-equalizing dropping funnel. To the flask were added 5.6 g (0.05 mol) of potassium tert-butoxide and 30 ml of DMSO and the dropping funnel charged with 6.7 g (0.025 mol) of tosylate 47. The contents of the funnel were slowly added to the flask which was kept at room temperature during the addition with the aid of an ice water bath. During the addition, which took approximately twenty minutes, the reaction mixture initially became greenish, then dark blue and finally dark brown. During this time 25 mm of pressure was applied to pump the volatile products out of the reaction mixture. After the addition was over full vacuum was applied for forty-five minutes. The volatile compounds collected in the gas traps were degassed and transferred to a small tube that was sealed and kept in the refrigerator

until separation was accomplished using a ten-foot Carbowax column. A less volatile fraction remained in the gas traps. The most volatile fraction ~3 g consisted of traces of dimethyl sulfide (CH_3SCH_3), an unidentified product in 4% yield, 3-vinylmethylenecyclobutane 48 in 40% yield and some tert-butyl alcohol formed during the reaction. An nmr of the less volatile fraction (~1.5 g) showed peaks characteristic of tert-butyl alcohol, DMSO and the tert-butyl ether derivative that resulted from direct displacement reaction of the tosylate 48 by tert-butoxide.

Compound 48:

ir (neat): 3040, 2268, 1681, 1639, 1410, 995, 913 and 877 cm^{-1}

nmr (CCl_4):	δ 2.40-3.00	broad multiplet	5H
	4.68	multiplet	2H
	4.90	doublets (J_{bc} = 9 cps)	1H
	4.92	doublets (J_{ac} = 18 cps)	1H
	5.62-6.25	broad multiplet	1H

Thermolysis of 3-Vinylmethylenecyclobutane (48)

Approximately 0.08 g of compound 48 was transferred to a 10 ml glass tube which was then sealed at room temperature. The tube was wrapped with glass wool and placed in a tube furnace at 240° for nine hours (probably more than sufficient). Spectral characteristics of the product indicated that compound 48 rearranged quantitatively to 4-methylenecyclohexene (40).[17]

Compound 49:

ir (neat): 3021, 2899, 2841, 1661, 1449-1418 and 889 cm^{-1}

nmr (CCl_4): δ 2.21 broad singlet 4H
2.71 broad singlet 2H
4.68 broad singlet 2H
5.61 broad singlet 2H

1-Vinylcyclobutene (65)

Compound 65 was obtained when 10 g (0.0244 mol) of ditosylate 28 in 20 ml of dried DMSO was slowly added (over a period of fifteen minutes) to a 250 ml reaction flask equipped with a mechanical stirrer and dry ice and liquid nitrogen traps connected to a vacuum line (50 mm). Before the addition the flask was charged with 20 ml of dried DMSO and 10.9 g (0.0973 mol) of potassium tert-butoxide (1.32 excess if 1 mol of 28 requires 3 mol of potassium tert-butoxide to generate 1 mol of 65). The reaction mixture changed from greenish to brown and the flask was maintained at room temperature using a cooling water bath. After the addition was completed full vacuum was applied for a period of forty-five minutes. The volatile products collected in the traps were identified as traces of dimethyl sulfide (CH_3SCH_3), 1-vinylcyclobutane (65) and tert-butyl alcohol. Separation was accomplished by gas chromatography using a ten-foot Carbowax column at 100°. The yield of 1-vinylcyclobutene (65) varied between 10 and 15% in three different runs.

The reaction mixture remaining in the reaction flask of one of the runs was extracted with 200 ml of ethyl ether and

200 ml of benzene. The ether extracts were acidified and washed twice with 50 ml of water. The organic layer was separated and the ether quickly removed by distillation. There remained a residue of 3.3 g which contained ethyl ether, cyclopropane-1,1-dimethyl di*tert*-butyl ether (86) and *tert*-butyl alcohol. The benzene extracts did not contain any 86. The amount of 86 recovered from the work-up of the reaction mixture was estimated at 1.27 g (30% yield).

The reaction mixture remaining in another run was additionally heated at 150° for twenty hours. The only major volatile product corresponded to dimethyl sulfide. No more compound 65 formed.

A variation on the reaction conditions was attempted by adding 0.01 mol of ditosylate 28 in 30 ml of DMSO to a mixture of 0.023 mol of potassium *tert*-butoxide and 0.04 mol of dimsyl anion at room temperature. The dimsyl anion was prepared by heating 0.04 mol of sodium hydride and 15 ml of dried DMSO at 75-80° for one hour under a nitrogen atmosphere. Compound 65 was observed but the yield was not improved.

Another variation was attempted by mixing the ditosylate with dimsyl anion before addition of potassium *tert*-butoxide. No volatile compounds were collected until the reaction mixture was heated at 55° for thirteen hours. No 65 was observed and only traces of 1,1-divinylcyclopropane 22 were detected along with *tert*-butyl alcohol, dimethyl sulfide and traces of other unidentified compounds.

Compound 65:

ir (NaCl plates): 3195, 2899, 2817, 985, 847 and 769 cm^{-1}

nmr (CCl_4):

δ 2.35-2.70	broad multiplet	4H
5.05	doublets (J_{df} = 10 cps)	1H
5.08	doublet (J_{ef} = 17.5 cps)	1H
5.86	broad singlet	1H
6.27	doublet of doublets (J_{df} = 10 cps, J_{ef} = 17.5 cps)	1H

uv: λmax 233 mμ (ϵ 15800) and λ216 mμ (ϵ 8500)

mass spectra (M/e): 80 (P), 79 and 77

Compound 86:

bp: 85°/18 mm or 63°/1 mm

ir (NaCl plates): 2941, 1471, 1387, 1361, 1233, 1199, 1075, 1020, 952 and 893-870 cm^{-1}

nmr (CCl_4):

δ 0.32	singlet	4H
1.12	singlet	18H
3.14	singlet	4H

Thermolysis of 1-Vinylcyclobutene 65

Compound 66, 2-vinylbutadiene, was produced essentially quantitatively when 0.1 g of 65 was placed in a 900 ml pyrolysis tube, sealed under vacuum, and heated at 210° for three hours. Purification was accomplished using a fifteen-foot Carbowax column at 115°.

ir (CCl_4): 3077, 2985, 1587, 1418, 1379, 999, 923, 913 and 892 cm^{-1}

nmr (CCl_4):	δ 5.10-5.35	broad multiplet	6H
	5.54	broad singlet	
	6.20-6.80	doublet of doublets	2H

uv: λmax 208 mμ (ϵ 13400) and λ233 (ϵ 9700)

mass spectra (m/e): 80 (P), 79 and 77

Reaction of 1-Vinylcyclobutene 65 with TCNE

To an nmr tube containing 0.03 g of compound 65 in a mixture of CCl_4 and C_6D_6 were added small portions of tetracyanoethylene (TCNE). The peaks corresponding to 65 disappeared and those corresponding to the Diels-Alder adduct appeared (similar to the reaction of 23 with TCNE).

nmr (C_6D_6 + CCl_4):	δ 1.3-2.5	multiplet	7H
	2.5-3.2	multiplet	
	4.5-4.7	multiplet	1H

Mixed Sulfoxide 77

The mixed sulfoxide 77 was prepared by reacting n-hexyl tosylate with dimsyl anion. A 200 ml three-necked flask was equipped with a magnetic stirrer for continuous stirring throughout the reaction, a dried nitrogen inlet and outlet to maintain positive pressure of nitrogen, and a rubber serum cap. The flask was charged with 13 g (0.32 mol) of sodium hydride 56% oil dispersion; the sodium hydride dispersion was washed three times with 50 ml portions of dried pentane to eliminate the oil. Approximately 50 ml of dried DMSO was injected through the serum cap and the mixture heated to 75-80° for one and one-half hours until hydrogen evolution ceased, an indication that the dimsyl anion formation was

completed. The reaction flask was then cooled down to room temperature and 23.4 g (0.091 mol) of crude n-hexyl tosylate in 40 ml of DMSO was slowly injected over a period of twenty minutes to the reaction flask containing the freshly prepared dimsyl anion. The reaction mixture was cooled down to room temperature during the tosylate addition with the aid of an ice water cooling bath. A change of color from light red to purple was observed during the addition. Stirring was continued for twenty minutes after the addition was completed. Then 150 ml of water was slowly added, maintaining the reaction flask at room temperature, and the purple solution became yellow-brown. The reaction mixture was extracted twice with 250 ml of ethyl ether, the organic layer separated, dried over Na_2SO_4 and the ether distilled off; 13.3 g of crude liquid (85% yield) which showed the spectral characteristics of the sulfoxide 77 remained.

The crude, oily n-hexyl tosylate used in the above reaction was prepared using a procedure similar to the one followed for the preparation of tosylate 47 in 92% yield.

Compound 77:

ir (NaCl plates): 2899, 2841, 1653, 1449 and 1031 cm^{-1}

nmr (CCl_4):	δ 0.73-1.70	multiplet	13H
	2.49	singlet	3H
	2.66	triplet	2H

n-Hexyl Tosylate:

ir (NaCl plates): 2976, 2924, 1637, 1471, 1370, 1196, 1183, 1099, 935 and 820 cm^{-1}

nmr (CCl_4):	δ 2.83-1.70	multiplet	11H
	2.44	broad singlet	3H
	3.98	triplet	2H
	7.32	doublet	2H
	7.75	doublet	2H

Mixed Sulfoxide 78

This sulfoxide was prepared in 71% yield following a method similar to the one described for the preparation of the mixed sulfoxide 77 by reacting benzylcarbinyl tosylate with dimsyl anion. The nmr and ir spectra of the mixed sulfoxide 78 were identical to the spectra of an authentic sample of 78 prepared by the reaction of styrene and dimsyl anion.[52]

Mixed Sulfoxide 79

A method similar to the one followed in the preparation of 77 was used in trying to obtain 79. Benzyl tosylate[36] was reacted with dimsyl anion and the reaction product worked up. The crude product contained trans-stilbene[53] in ~10% yield and mixed sulfoxide 79 in ~30% yield. The low yield of the reaction was probably due to the unstable benzyl tosylate that partially polymerized after its preparation.[36]

Cyclopropylcarbinyl Tosylate 82[54]

In a 200 ml round-bottomed flask was placed 0.06 mol of cyclopropylcarbinol in 45 ml of anhydrous ether. The temperature of the flask was lowered to -6° using an ice-salt bath and 0.06 mol of p-toluenesulfonyl chloride was added to the ether solution followed by 1.0 g of powdered potassium hydroxide over a period of one hour, maintaining the temperature at

-6°. Then a stopper was put on the mouth of the flask and the flask was kept in a freezer (-18°) for five hours. Ice and water were added to the reaction mixture; the organic layer separated and the water layer was extracted with cold ethyl ether. The ether layers were combined, maintained at ~0° and dried with $MgSO_4$. An oily residue remained after quick evaporation of the ether. The crude tosylate obtained was contaminated with p-toluenesulfonyl chloride; the yield of tosylate was estimated at ~60%. Attempts to prepare solid samples of tosylate 82 were fruitless.[54]

Reaction of 82 with Potassium tert-Butoxide in DMSO

To the crude tosylate 82 (~0.036 mol) in 30 ml of dried DMSO was added 0.11 mol of powdered potassium tert-butoxide, using a system similar to the one used for the preparation of 1,1-divinylcyclopropane (22). The volative products collected in the gas traps cooled at -190° with liquid nitrogen were identified as methylenecyclopropane and cyclobutene (in an approximate ratio of 1/1), along with traces of isobutene, which had been observed in the preparation of methylenecyclopropane from 2-methylpropenyl chloride and sodium amide.[55]

Cyclopropylcarbinyl Tosylate-d_2 (82-d_2)

This compound was prepared using a procedure similar to the one followed for the preparation of 82, but using cyclopropylcarbinol-d_2 (7-d_2).

nmr (CD_3Cl):	δ 0.05-0.80	multiplet	4H
	0.80-1.50	multiplet	1H
	2.43	singlet	3H
	3.90	doublet	2H
	7.10-8.00	doublets	4H

Reaction of Tosylate 82-d_2 with Potassium tert-Butoxide

A procedure similar to the one used for the reaction of 82 with potassium tert-butoxide was followed. An nmr of the cyclobutene formed showed an allyl to vinyl ratio of approximately 2.3/2 (Table VI).

Cyclopropylcarbinyl p-Nitrobenzoate (83)

This compound[56] was prepared in 80% yield from the reaction of p-nitrobenzoyl chloride and cyclopropylcarbinol in pyridine.

nmr ($CD_3\overset{O}{\overset{\|}{C}}CD_3$):	δ 0.35-0.75	multiplet	4H
	0.95-1.60	multiplet	1H
	4.25	doublet	2H
	8.38	singlet	4H

Reaction of 83 with Potassium tert-Butoxide

A system similar to the one used for the reaction of 82 with potassium tert-butoxide was followed. To 2.5 g (0.0117 mol) of 83 in 7 ml of DMSO was slowly added 6 g (0.0535 mol) of powdered potassium tert-butoxide. The reaction flask was kept at room temperature and vacuum was applied (20 mm) during the addition. The milky reaction mixture changed colors from purple to brown during the addition. No volatile compounds were collected in the gas traps during the addition nor after full vacuum was applied for an additional forty-five minutes. The mixture remaining in the reaction flask was treated with water and extracted with three 200 ml portions of ether. The ether extracts were combined, dried over $MgSO_4$ and the ether quickly rotor water pump evaporated. About 1 g of residue remained which was identified as a mixture of tert-butyl

alcohol and cyclopropylcarbinol: both are hydrolysis products formed during the work-up of the mixture remaining in the reaction flask.

Reaction of Cyclopropane-1,1-dicarbinyl Dibromide 29 with Potassium *tert*-Butoxide

We used the same system and procedure as the one used for the preparation of 1-vinylcyclobutene (65) from the reaction of cyclopropane-1,1-dicarbinyl ditosylate (28) in DMSO with potassium *tert*-butoxide. The volatile products collected in the gas traps did not indicate the presence of any 1-vinylcyclobutene, the major volatile product being dimethyl sulfide and traces of at least three more compounds. The contents of the reaction flask were treated with ice water and extracted with ether; the ether layers were combined, dried over $MgSO_4$ and the ether evaporated. The residue remaining after this treatment consisted only of *tert*-butyl alcohol and cyclopropane-1,1-dicarbinyl dimethyl ether (86) (bp 85°/18 mm or 63°/1 mm) which was similarly obtained in the reaction of 28 with potassium *tert*-butoxide. The yield of recovered 86 was estimated at ~40%.

Methyl, 1-Methylcyclopropanecarboxylate

This compound was prepared from the reaction of methyl methacrylate with diazomethane.[57]

ir (NaCl plates): 2950, 1730, 1468, 1437, 1342, 1527, 1198, 1163, 1047, 1031, 957, 877, 763 and 758 cm^{-1}

nmr (neat):	δ 0.63	multiplet	2H	(symmetrical)
	1.12	multiplet	2H	
	1.28	singlet	3H	
	3.57	singlet	3H	

1-Methylcyclopropylcarbinol[57]

This compound was prepared in ~80% yield from the $LiAlH_4$ reduction of methyl, 1-methylcyclopropanecarboxylate.[57]

bp: 126-127°/739 mm

ir (NaCl plates): 3333, 3030-2857, 1449, 1429, 1387, 1070-1010, 919, 862 and 724 cm^{-1}

nmr (CCl_4):	δ 0.25	multiplet	2H	(symmetrical)
	0.37	multiplet	2H	
	1.13	singlet	3H	
	2.25	broad singlet	1H	
	3.21	singlet	2H	

1-Methylcyclopropylcarbinyl Bromide (87)[58]

A 200 ml three-necked flask was equipped with a magnetic stirrer, a pressure-equalizing dropping funnel and a nitrogen inlet and outlet to maintain a positive nitrogen pressure during the reaction. The reaction flask was placed in an ice water bath and then charged with 1.6 g (0.0187 mol) of 1-methylcyclopropylcarbinol, 20 ml of DMF, and 5.25 g (0.02 mol) of triphenyl phosphine. Bromine, contained in the dropping funnel, was added drop by drop until an orange color persisted after one minute of continuous stirring. The reaction was then immediately connected to a vacuum line and all the volatile products were collected in a 200 ml flask cooled in dry ice. To the volatile products were added 50 ml of pentane (bp 20-40°) and 10 ml of ice water. Two layers formed; the

organic layer was separated and the water layer washed with 50 ml of pentane. The pentane extracts were combined, dried over Na_2SO_4 and then the pentane was evaporated. The dark residue that remained was flash distilled to give 1 g (46% yield) of a slightly orange-tinted liquid which was identified as the bromide 87.

bp: $65^{\circ}/130$ mm

nmr (CCl_4): δ 0.58 singlet 4H
1.12 singlet 3H
3.23 singlet 2H

Reaction of 87 with Potassium *tert*-Butoxide

To 4.15 g (0.037 mol) of potassium *tert*-butoxide contained in a reaction flask was added 0.8 g (0.054 mol) of bromide 87 in 20 ml of dried DMSO, a set-up similar to previous reactions of bromides with potassium *tert*-butoxide, although the order of addition was inverted. The major volatile products were identified[59] as methylenecyclobutane (60) and 1-methylcyclobutene (89) along with a small amount of 1-methylcyclopropylcarbinyl methyl ether (88). Work-up of the contents of the reaction flask produced more mixed ether 88. Approximately 0.07 g (~20% yield) of a mixture of 60 and 89 (in a ratio of 2/1) were obtained. The yield of 88 recovered was estimated at 0.38 g (50% yield). An analytical sample of 88 was collected by gas chromatography using a ten-foot Carbowax column at 135°.

Compound 88:

ir (NaCl plates): 2950, 2874, 1456, 1389, 1361, 1212, 1078, 1027, 885 and 865 cm^{-1}

nmr (CCl_4):	δ 0.19	multiplet	2H	(symmetrical)
	0.31	multiplet	2H	
	1.04	singlet	3H	
	1.12	singlet	9H	
	3.05	singlet	2H	

Cyclopropylcarbinyl Methyl Bromide (90)

The preparation of 90 (containing traces of DMF) was accomplished in ~50% yield by reacting cyclopropylcarbinyl methyl alcohol[60] in DMF with triphenyl phosphine and bromine following the reaction procedure used for the preparation of 87.

bp:	$70^{\circ}/128$ mm			
nmr (CCl_4):	δ 0.40	multiplet	2H	(symmetrical)
	0.75	multiplet	2H	
	0.90-1.40	multiplet	1H	
	1.75	doublet	3H	
	3.37	quartet	1H	

Reaction of 90 with Potassium *tert*-Butoxide

The same set-up and reaction conditions as the ones used for the reaction of 87 with potassium *tert*-butoxide were used. The major volatile product corresponded to a 2/1 ratio of a mixture (~70% yield) of compounds 84[61] and 91.[62] Traces of other compounds collected in the gas traps corresponded to *tert*-butyl alcohol, dimethyl sulfide and mixed ether 92. No attempts were made to recover 92 from the nonvolatile reaction mixture remaining in the reaction flask after the volatile products were pumped out of the reaction mixture. An nmr of the volatile products did not show peaks that could be credited to 3-methylcyclobutene.[63]

Methylcyclobutyl Bromide (94)

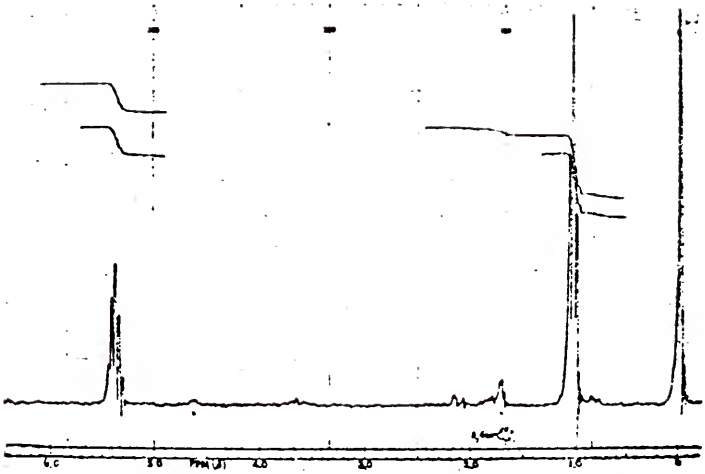
Unlike the reaction of 1-methylcyclopropylcarbinol with triphenyl phosphine and bromine that produced the bromide 87, the reaction of 1-methylcyclopropylcarbinol with phosphorous tribromide produced the rearranged bromide 94. In a flask protected from atmospheric moisture were placed 1.72 g (0.02 mol) of 1-methylcyclopropylcarbinol and 10 ml of anhydrous ether. The solution was cooled in a dry ice-acetone bath and 0.66 ml (0.007 mol) of phosphorous tribromide was slowly added while stirring. The mixture was allowed to reach room temperature and 2 ml of water was added. The ether layer separated and was washed with sodium bicarbonate and dried over drierite. The ether was removed and the dark residue was flash distilled to give 2 g of a colorless liquid containing the bromide 94 (which had been prepared[43] from the reaction of methylenecyclobutane and hydrobromic acid), along with traces of the bromide 87.

bp:	$71^{\circ}/90$ mm (lit.[43b] $111\text{-}112^{\circ}$)		
ir (NaCl plates):	2950, 2865, 1439, 1429, 1372, 1242, 1125, 926-889, 787 and 690 cm^{-1}		
nmr (CCl_4):	δ 1.80-3.00	multiplet	6H
	1.95	singlet	3H

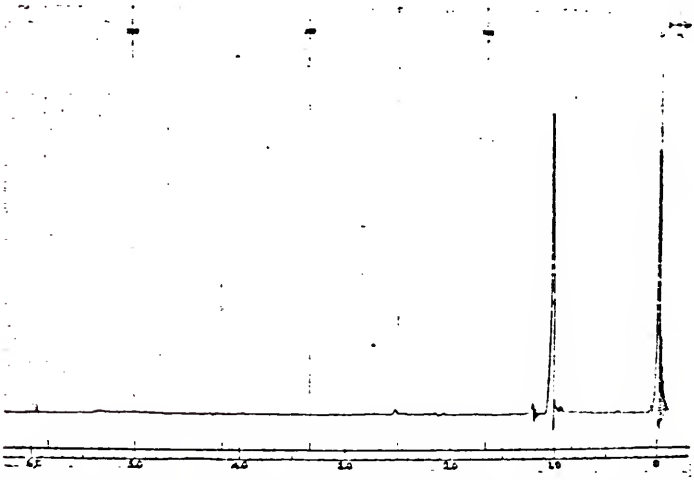
APPENDIX

nmr and ir Spectra

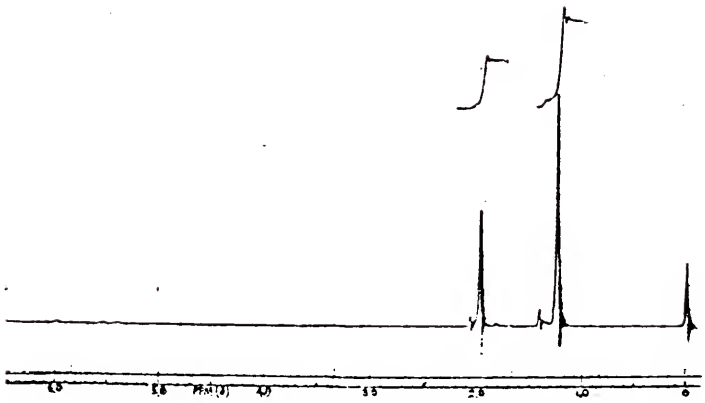
(Solvents and absorption positions are recorded in the Experimental Section.)



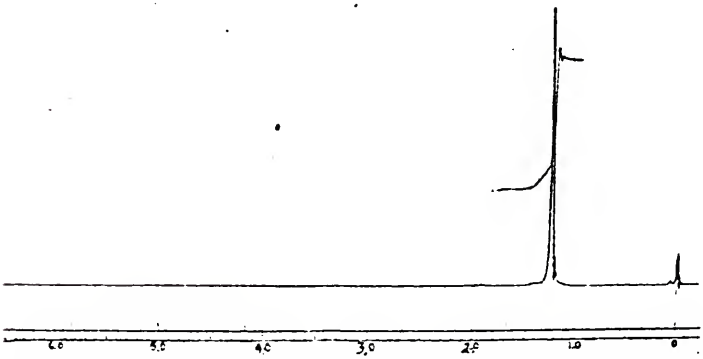
Spectrum 1. nmr of methylenecyclopropane (2)[55]



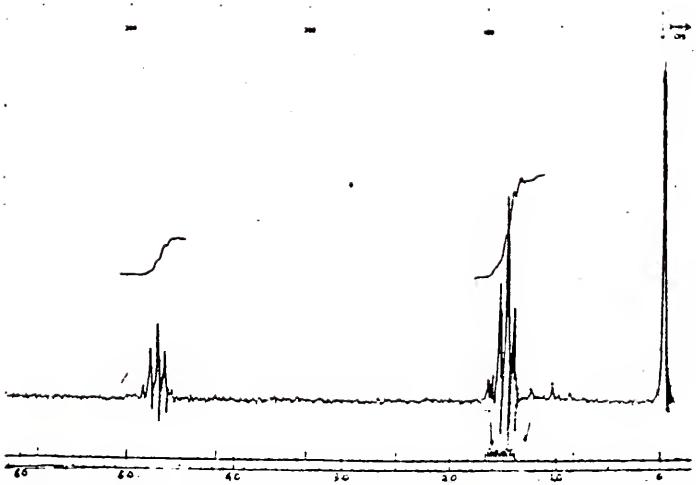
Spectrum 2. nmr of dideuteriomethylenecyclopropane (2-d_2)



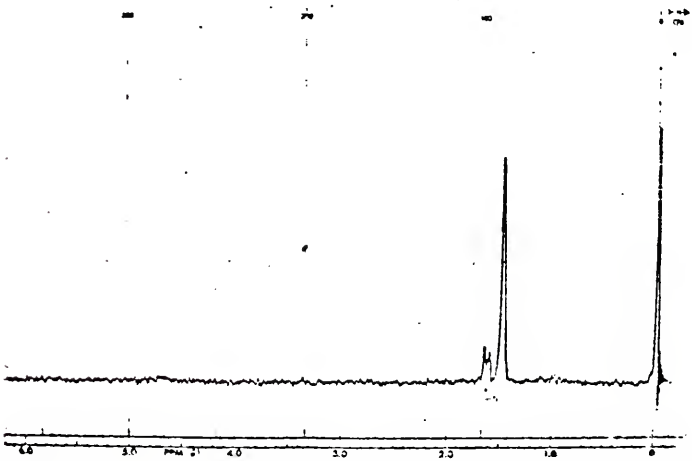
Spectrum 3. nmr of dibromospiropentane (3)



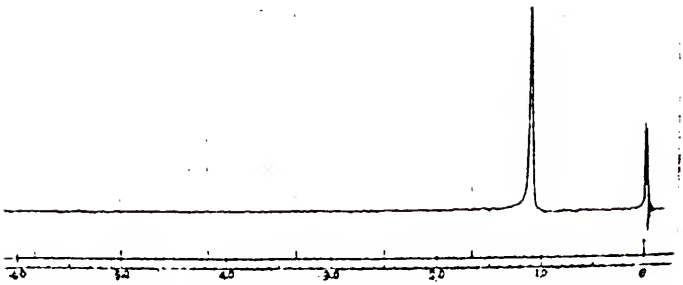
Spectrum 4. nmr of dibromospiropentane-d_2 (3-d_2)



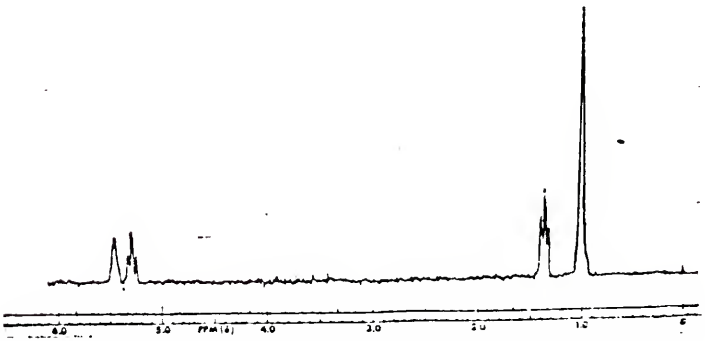
Spectrum 5. nmr of vinylidenecyclopropane (4)



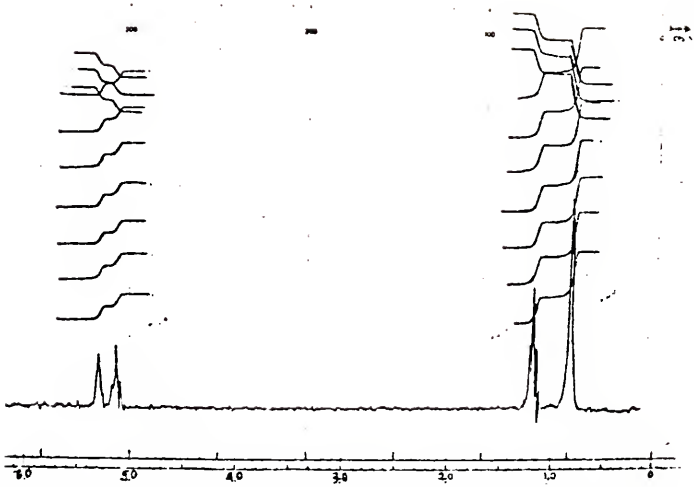
Spectrum 6. nmr of dideuteriovinylidenecyclopropane (4-d_2)



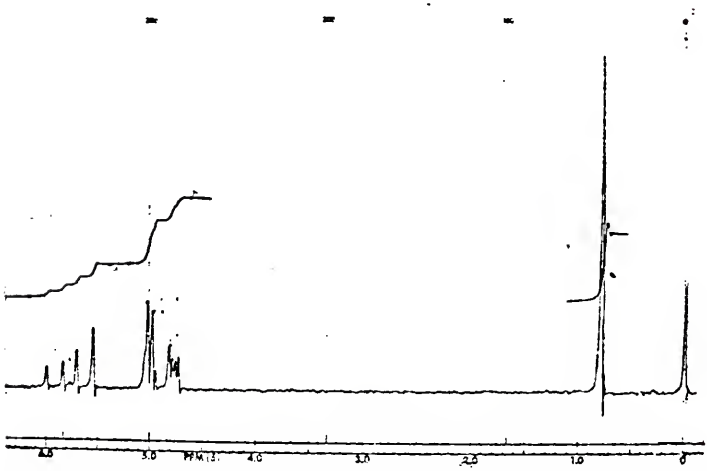
Spectrum 7. nmr of dideuteriobiscyclopropylidene (1-d_2)



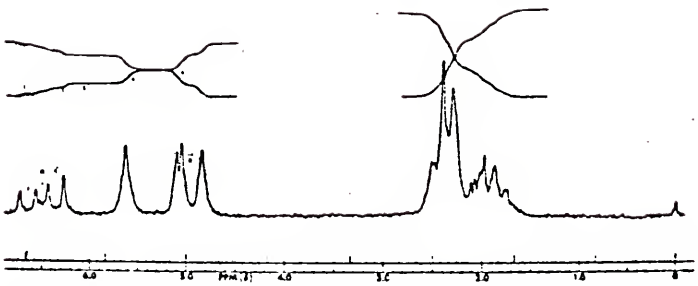
Spectrum 8. nmr of methylenespiropentane (6) in C_6D_6



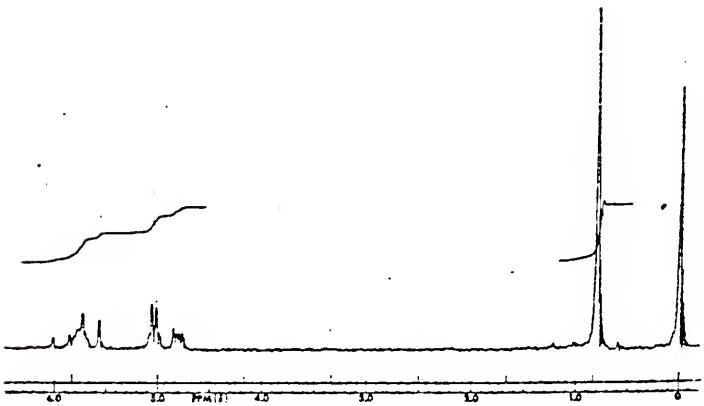
Spectrum 9. nmr of mixture of dideuterated methylenespiropentanes (x, y, z)



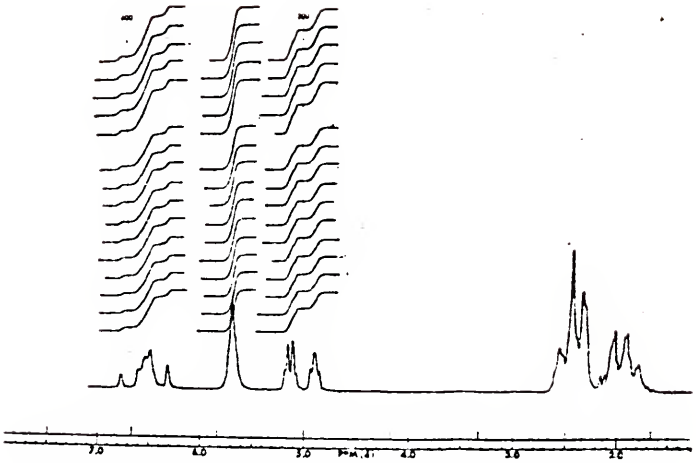
Spectrum 10. nmr of 1,1-divinylcyclopropane (22)



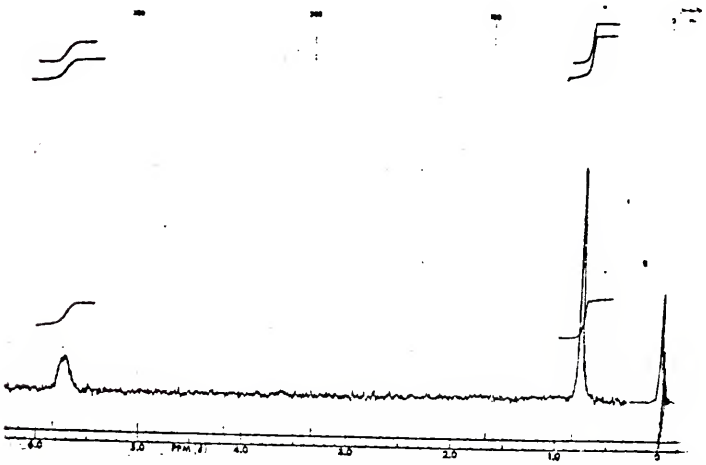
Spectrum 11. nmr of 1-vinylcyclopentene (23)



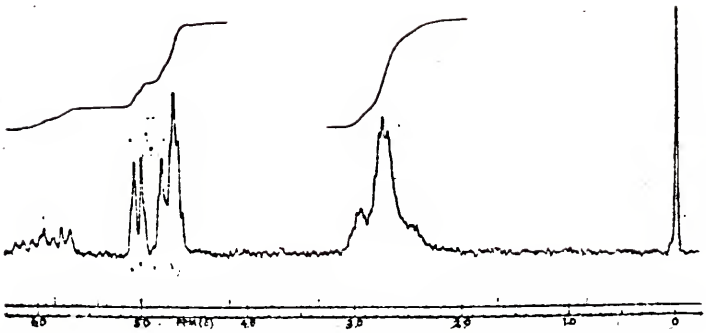
Spectrum 12. nmr of 1,1-divinylcyclopropane-d_2 (22-d_2)



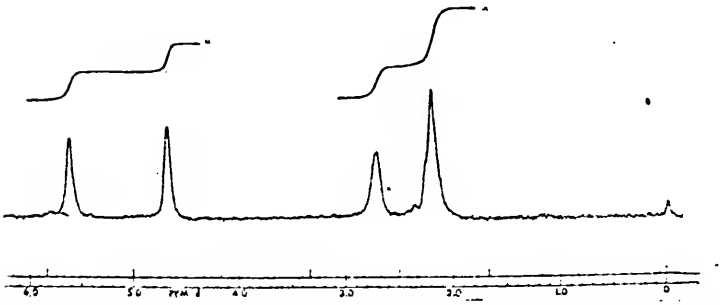
Spectrum 13. nmr of mixture of dideuterated 1-vinylcyclopentenes ($\underline{x}_1$, $\underline{y}_1$)



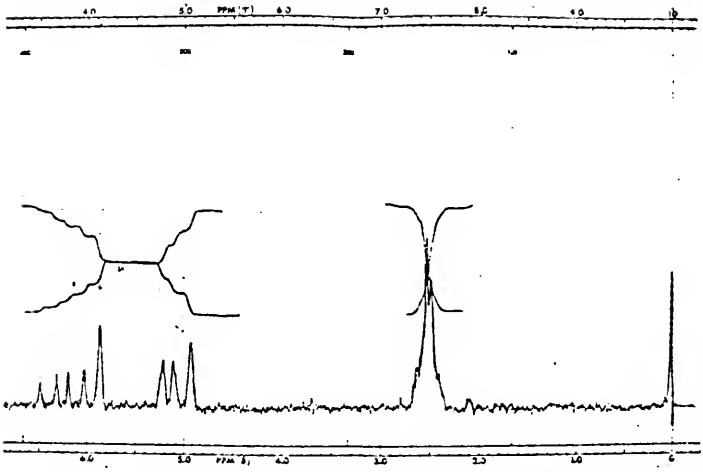
Spectrum 14. nmr of 1,1-divinylcyclopropane-d_4 ($\underline{22}$-d_4)



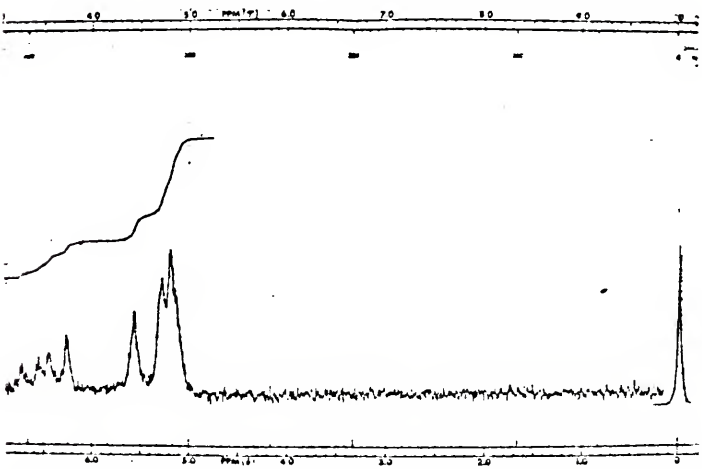
Spectrum 15. nmr of 3-vinylmethylenecyclobutane (48)



Spectrum 16. nmr of 4-methylenecyclohexene (49)

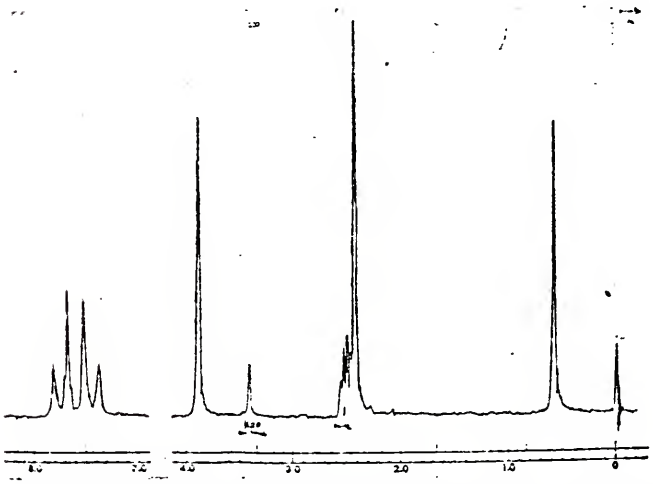


Spectrum 17. nmr of 1-vinylcyclobutene (65)

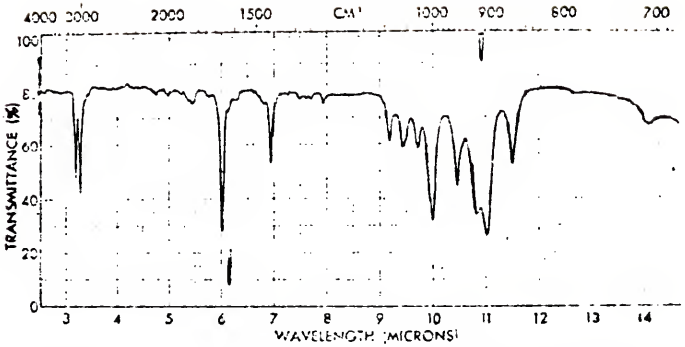


Spectrum 18. nmr of 2-vinylbutadiene (66)[31]

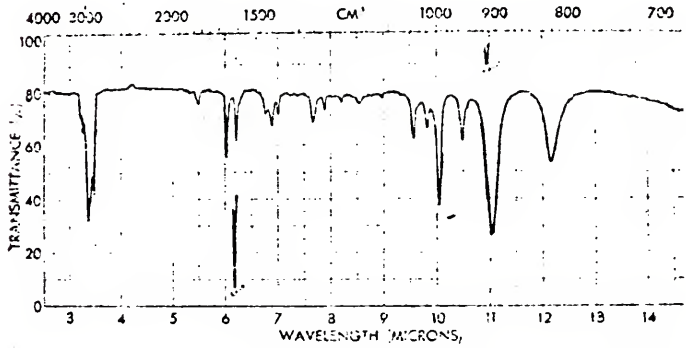
Spectrum 19. nmr of cyclopropylcarbinyl bromide-d_2



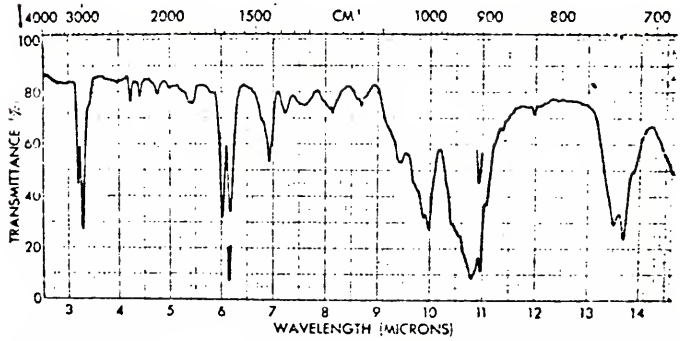
Spectrum 20. nmr of cyclopropane-1,1-dicarbinol di-p-toluenesulfonate (28) in DMSO-d_6



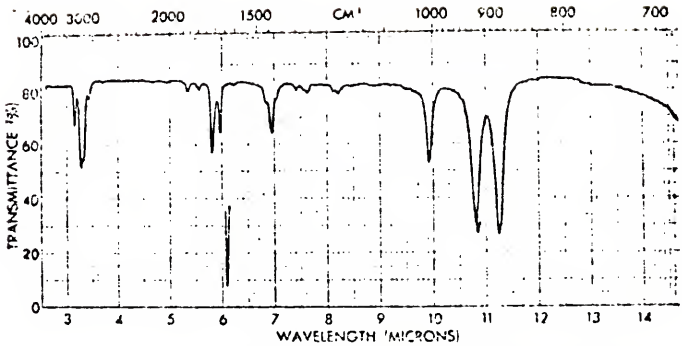
Spectrum 21. ir of 1,1-divinylcyclopropane (22)



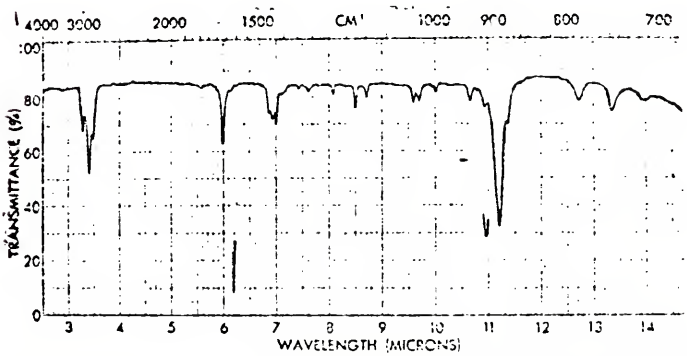
Spectrum 22. ir of 1-vinylcyclopentene (23)



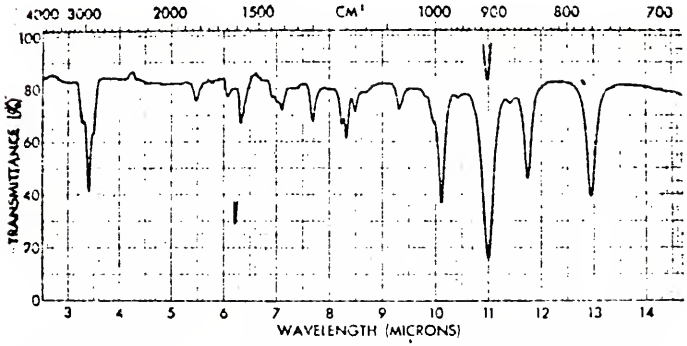
Spectrum 23. ir of 1,1-divinylcyclopropane-d_2 (22-d_2)



Spectrum 24. ir of 3-vinylmethylenecyclopropane (48)



Spectrum 25. ir of 4-methylenecyclohexene (49)



Spectrum 26. ir of 1-vinylcyclobutene (65)

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He will return to his native Colombia upon completion of work toward the degree of Doctor of Philosophy and will join the staff of the Chemistry Department of the Universidad del Valle in Cali, where he will teach and develop research as demanded by the needs of his developing country.

I certify that I have read this study and that in my opinion it conforms to acceptable standards of scholarly presentation and is fully adequate, in scope and quality, as a dissertation for the degree of Doctor of Philosophy.

William R. Dolbier, Chairman
Associate Professor of Chemistry

I certify that I have read this study and that in my opinion it conforms to acceptable standards of scholarly presentation and is fully adequate, in scope and quality, as a dissertation for the degree of Doctor of Philosophy.

John A. Zoltewicz
Associate Professor of Chemistry

I certify that I have read this study and that in my opinion it conforms to acceptable standards of scholarly presentation and is fully adequate, in scope and quality, as a dissertation for the degree of Doctor of Philosophy.

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Associate Professor of Chemistry

I certify that I have read this study and that in my opinion it conforms to acceptable standards of scholarly presentation and is fully adequate, in scope and quality, as a dissertation for the degree of Doctor of Philosophy.

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Associate Professor of Chemistry

I certify that I have read this study and that in my opinion it conforms to acceptable standards of scholarly presentation and is fully adequate, in scope and quality, as a dissertation for the degree of Doctor of Philosophy.

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Professor of Chemical Engineering

This dissertation was submitted to the Department of Chemistry in the College of Arts and Sciences and to the Graduate Council, and was accepted as partial fulfillment of the requirements for the degree of Doctor of Philosophy.

March, 1973

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